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Feature Article

Recent progress in controlled radical polymerization of *N*-vinyl monomers

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ABSTRACT

This review summarizes recent advances in the controlled radical polymerization of *N*-vinyl monomers, such as *N*-vinylcarbazole, *N*-vinylindole derivatives, *N*-vinylpyrrolidone, *N*-vinylcaprolactam, *N*-vinylformamide, *N*-vinylacetoamide derivatives, *N*-vinyl(na)phthalimides, *N*-vinylimidazolium salts, and *N*-vinyltriazoles. Recent significant progress of controlled radical polymerization of these *N*-vinyl monomers has allowed for the synthesis of well-defined functional polymers having various architectures, including block copolymers, branched polymers (stars, star block copolymers, miktoarm star copolymers, and graft copolymers), and hybrids. Characteristic properties, assembled structures, and three-dimensional architectures of these functional polymers derived from *N*-vinyl monomers are briefly introduced.

Contents

1. Introduction

Controlled radical polymerization (also known as controlled/"living" radical polymerization or reversible deactivation radical polymerization) has facilitated the synthesis of various functional polymers with predetermined molecular weights, narrow molecular weight distribution, and controlled architectures, such as star and branched polymers, block and graft copolymers, using a facile approach. The method combines the benefits of the robust nature of conventional radical polymerization with the capability to prepare well-defined macromolecular architectures common to living polymerization

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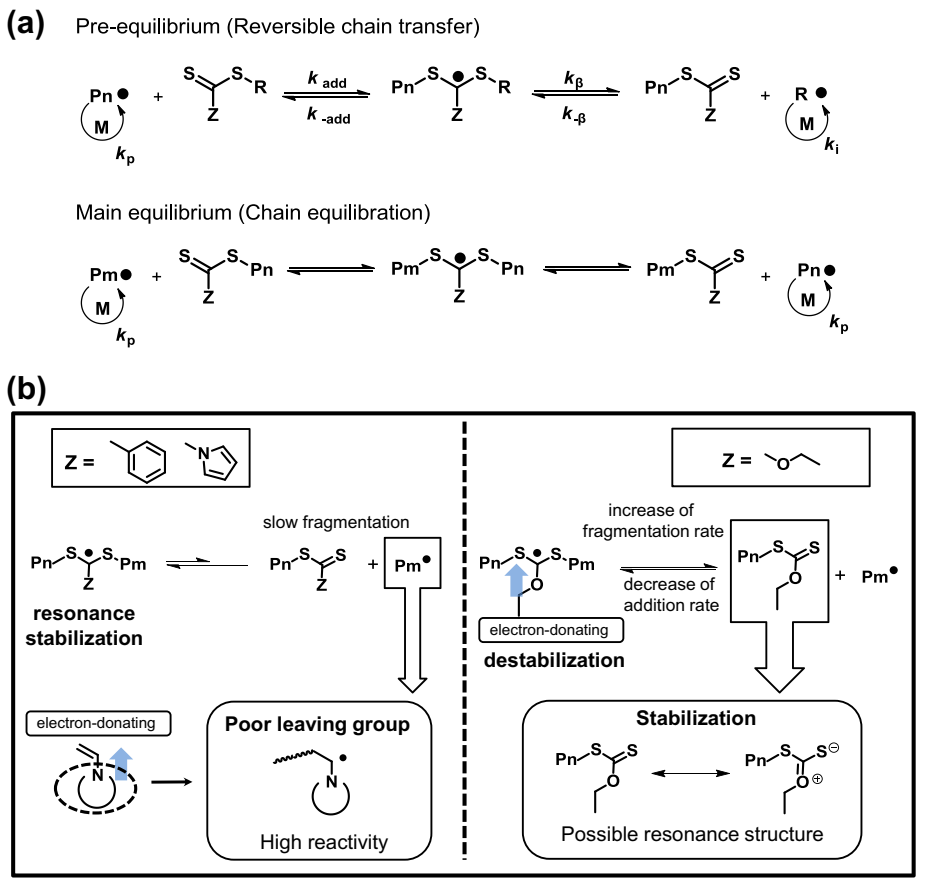
techniques. The representative controlled radical polymerization includes nitroxide-mediated polymerization (NMP) [1,2], atom transfer radical polymerization (ATRP) or transition metal-catalyzed living radical polymerization [3–7], reversible addition–fragmentation chain transfer (RAFT) polymerization [8–26], single electron transfer-living radical polymerization (SET-LRP) [27], organoheteroatom-mediated living radical polymerization [28], and organometallic-mediated radical polymerization [29,30]. All these systems are based on establishing a rapid dynamic equilibration between a minute amount of growing free radicals and a large majority of dormant species, and are more tolerant of functional groups and impurities. Such controlled radical polymerization methods have become key tools for polymer synthesis, especially for synthesizing complex polymers with well-defined structures.

One of the important features of controlled radical polymerization is its versatility to monomer choice and polymerization conditions. A wide variety of vinyl monomers with various functional groups have been applied for controlled radical polymerization. Similar to styrene (St), (meth)acrylate, (meth)acrylamide derivatives, *N*-vinyl monomer has a multiplicity of chemical structures, which lead to the versatility and usability of *N*-vinyl monomers for the production of functional polymers having various properties and functions. Despite a variety of functional polymers were prepared via conventional free radical polymerization of *N*-vinyl monomers, controlled radical polymerization of nonconjugated *N*-vinyl monomers had been difficult until recent years. This is due to the fact that the generated radical species are highly reactive due to their nonconjugated nature (lack of resonance stabilization) and strong electron donating pendant groups. Hence, unfavorable chain transfer and termination reactions could not be suppressed, due to the high reactivity of the propagating radicals derived from *N*-vinyl monomers. Recent progress of controlled radical polymerization, particularly RAFT/MADIX (macromolecular design via the interchange of xanthates) process, allowed for the synthesis of well-defined polymers by radical polymerization of nonconjugated *N*-vinyl monomers.

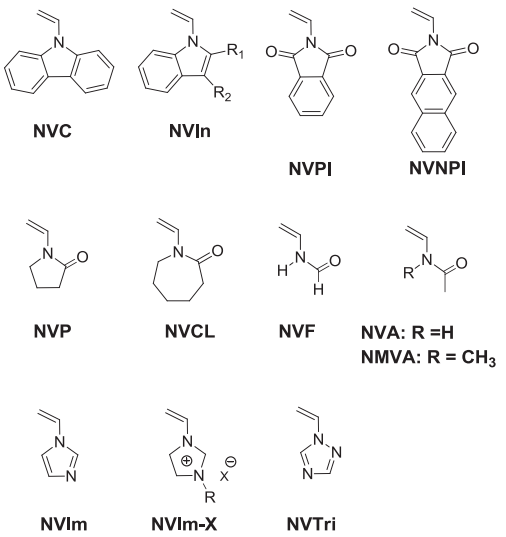
The RAFT process is generally accomplished by performing a radical polymerization in the presence of a thiocarbonylthio compound, such as a dithioester, dithiocarbamate, trithiocarbonate, or xanthate, all of which act as reversible chain transfer agents (CTAs). When xanthates are employed, the terminology MADIX is frequently used to describe the process [31–33]. Both the MADIX and RAFT processes are based on the generally accepted reversible addition–fragmentation chain transfer mechanism between an active and a dormant species. Beyond the general advantages of RAFT process, there remain challenges to be addressed, involving the controlled polymerization of more challenging monomer systems [26]. The development of a new *N*-vinyl monomer family, which is applicable for controlled radical polymerization, would represent a significant advance in the field of functional polymeric materials. To achieve control of the radical polymerization via the RAFT/MADIX process, a delicate balance of the forward and reverse rates of addition (k_{add} and k_{-add}) and fragmentation (k_{β} and $k_{-\beta}$), together with the rates of reinitiation (k_i) and propagation (k_p), is required (Scheme 1a). Because the propagating radical of *N*-vinyl monomer is a poor homolytic leaving group, the fragmentation of the RAFT-adduct radical (intermediate radical) is thought to be very slow when dithioesters are used, resulting in insufficient control of the polymerization. In general, the use of the dithiobenzoates in such system leads to more extensive inhibition times and/or the formation of broad molecular weight distribution products. In contrast, the xanthate-type CTA is useful for achieving controlled radical polymerization of *N*-vinyl monomer, because it increases electron density at the radical center, which may lead to the destabilization of the RAFT-adduct radicals relative to the normal dithioester-type CTA and an increase in the fragmentation rate. The electron-donating *O*-alkyl substituents may lead to stabilization of the thiocarbonyl product of fragmentation through their conjugation with the C=S double bond, as shown in Scheme 1b. This lowers the rate of addition of the propagating radicals to the sulfur atom, and consequently the overall rate of chain transfer [10,34–36]; whereas the introduction of electron-withdrawing groups in the Z moiety leads to an increase in the rate of addition [35]. Dithiocarbonates (xanthates) were also reported to be useful for controlling the radical polymerization of highly reactive *O*-vinyl monomers, such as vinyl acetate (VAc) [31,37,38,39,40].

This review highlights recent developments in controlled radical polymerization of nonconjugated *N*-vinyl monomers, such as *N*-vinylcarbazole (NVC), *N*-vinylindole (NVIn) derivatives, *N*-vinylpyrrolidone (NVP), *N*-vinylcaprolactam (NVCL), *N*-vinylformamide (NVF), *N*-vinylacetoamide (NVA) derivatives, *N*-vinylphthalimide (NVPI), *N*-vinylnaphthalimide (NVNPI), *N*-vinylimidazole (NVIm), *N*-vinylimidazolium salts (NVIm-X), and *N*-vinyltriazoles (NVTri), as shown in Scheme 2. Among various controlled radical polymerizations, RAFT polymerization is one of the most useful approaches to attain controlled character of the polymerization of nonconjugated *N*-vinyl monomers. Representative CTAs used for RAFT polymerization of the *N*-vinyl monomers are summarized in Schemes 3 and 4.

Here, we will mainly focus on RAFT polymerization of nonconjugated *N*-vinyl monomers and their applications for the controlled synthesis of functional polymers having various architectures, such as block and graft copolymers, alternating and gradient copolymers, star and branched polymers, and hybrids. Other controlled radical polymerizations, such as NMP, ATRP, SET-LRP, organoheteroatom-mediated living radical polymerization, and cobalt-mediated radical polymerization, are also useful systems to achieving controlled radical polymerization of some *N*-vinyl monomers, which are briefly introduced in this review. The block copolymers that are discussed herein are block copolymers composed of two different nonconjugated *N*- and *O*-vinyl monomers, block copolymers composed of "more activated" and "less activated" monomers, rod-coil type block copolymers, and block copolymers derived from vinyl monomer and cyclic monomer, in which at least one segment is formed by controlled radical polymerization of *N*-vinyl monomers. Combination of two different polymerization techniques (RAFT and ATRP, RAFT and NMP, RAFT and ring-opening polymerization, and so on) has been



Scheme 1. (a) Basic reaction steps of reversible addition–fragmentation chain transfer (RAFT) process and (b) proposed mechanism of xanthate-mediated controlled radical polymerization of *N*-vinyl monomers.

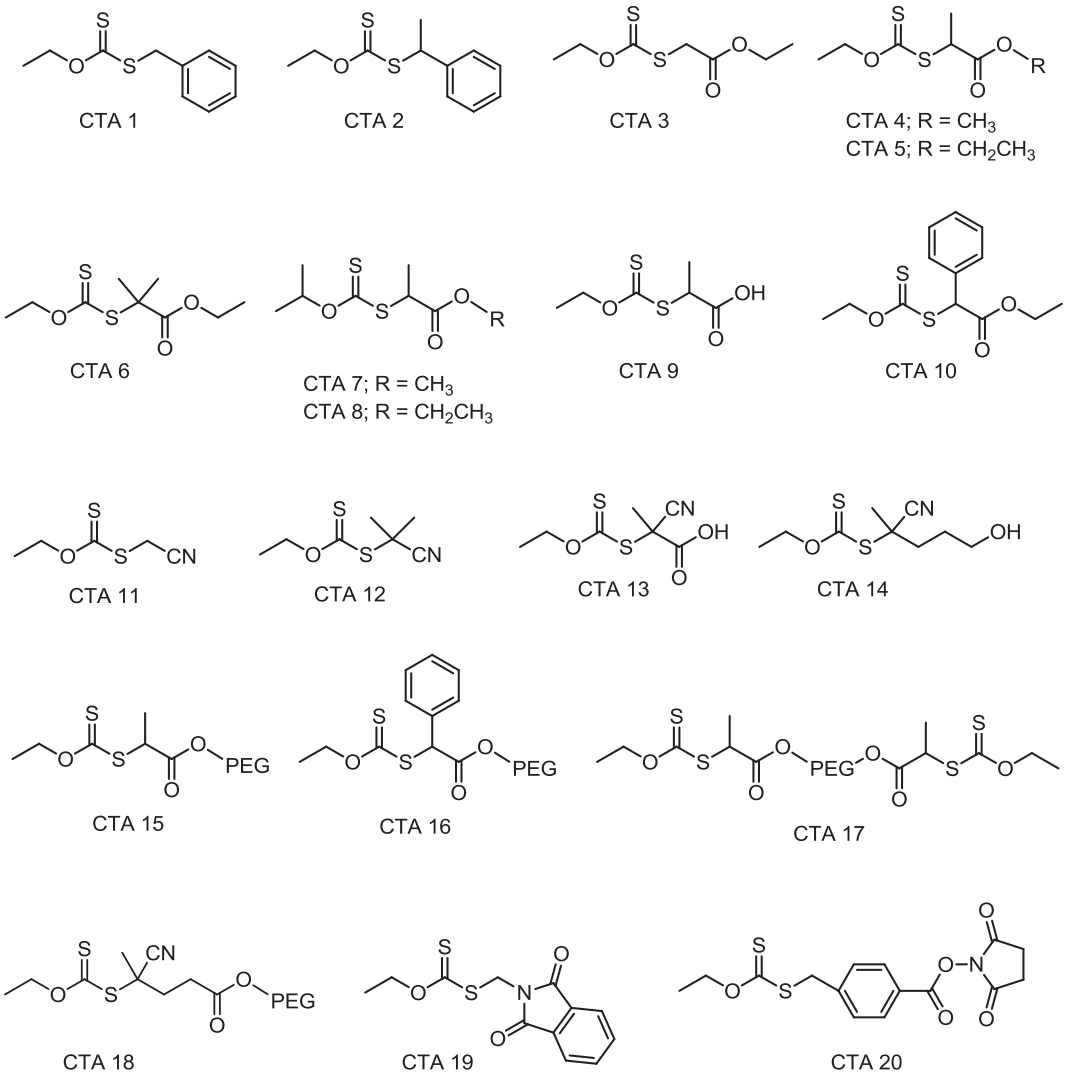


Scheme 2. Representative examples of nonconjugated *N*-vinyl monomers used for controlled radical polymerizations.

frequently employed for the synthesis of these block copolymers derived from *N*-vinyl monomers. Effective end-group transformation of the first block is an important step to produce well-defined block copolymers. We will also highlight recent results in the controlled synthesis of branched polymers, such as star polymers, star block copolymers, miktoarm star copolymers, and hybrids obtained by controlled radical polymerization of *N*-vinyl monomers.

2. *N*-vinylcarbazole (NVC) and *N*-vinylindole (NVIn)

Poly(NVC) was the first and most widely studied polymeric photoconductor. Numerous studies have been devoted to carbazole-containing polymers, due to their attractive features, such as hole-transporting, high charge-carrier mobility, and electroluminescent properties [41]. For several decades, there has been a great demand for the development of novel carbazole-containing polymers for realizing various optoelectrical applications, such as polymeric light emitting diodes, organic photorefractive materials, and photovoltaic devices. NVC, a strong basic monomer, undergoes facile cationic polymerization with almost all cationic initiators to give poly(NVC). Free radical initiators, such as azo compounds and peroxides, readily polymerize NVC, and radical polymerization was used in manufacturing the polymer [41]. The living cationic polymerization of NVC with hydrogen iodine has also been reported [42]. Many factors, such as chemical structures,

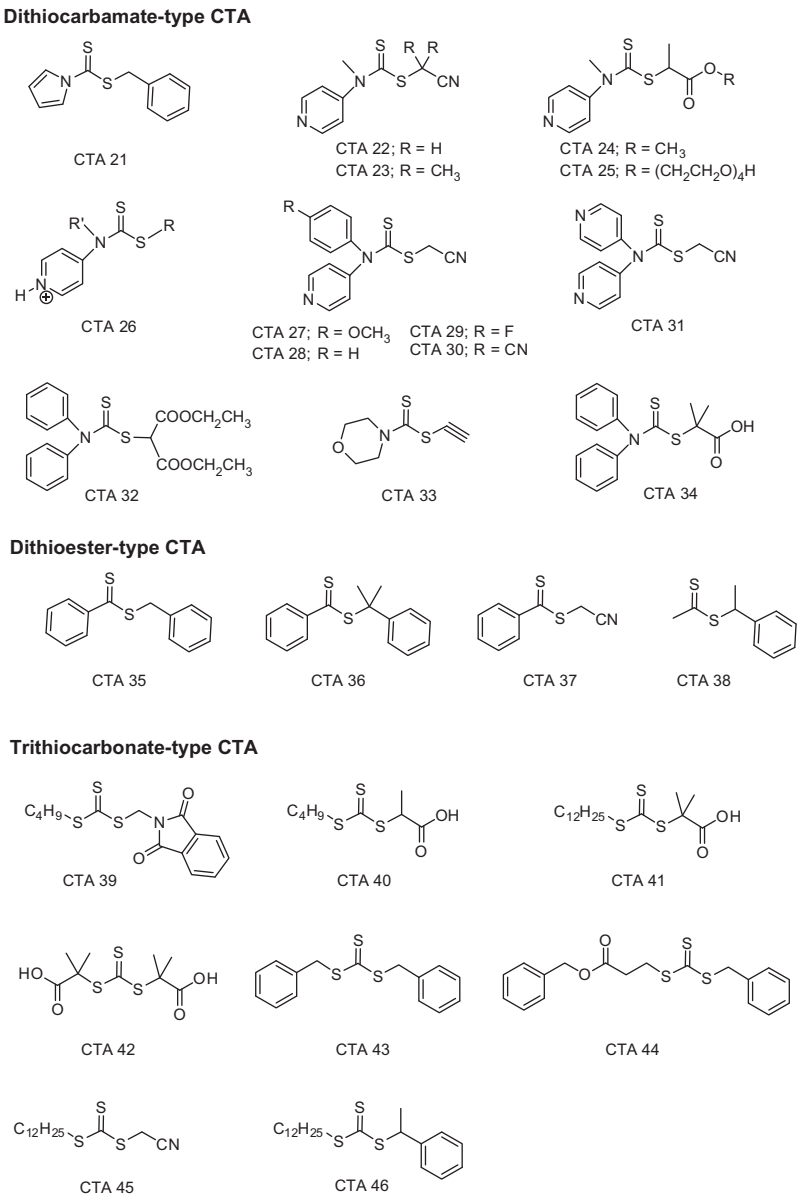


Scheme 3. Structures of xanthate-type chain transfer agents (CTAs) used for RAFT polymerization of nonconjugated *N*-vinyl monomers.

polymer architectures, conformation, location and stacking of the carbazole units, play a crucial role in manipulation of the properties and in several practical applications. However, it was difficult to control the molecular weights and their architectures, because most of these polymers with pendant carbazolyl groups have been synthesized by conventional radical polymerization. To manipulate unique electronic and photonic functions, it is desirable to establish precise synthetic methods to control molecular weight, polydispersity, topology, composition, and functions. Synthesis of complex polymers with carbazole moieties using controlled radical polymerization of various carbazole-containing monomers, such as NVC, St and (meth)acrylate derivatives, can be found in our recent review [43]. In contrast to nonconjugated NVC ("less activated" monomer), various St and (meth)acrylate derivatives having carbazole moieties, which belong to conjugated monomer ("more activated" monomer), have been traditionally employed for the controlled synthesis of carbazole-containing polymers with various architectures. The use of RAFT polymerization for the synthesis of various optoelectronic polymers was recently reviewed by Moad et al. [44].

The difficulties in adapting controlled radical polymerization to NVC is be based on the fact that the NVC propagating radical is relatively unstable and thus highly reactive, mainly because of the electron-donating carbazolyl pendant ($Q = 0.26$, $e = -1.29$) [45], leading to a tendency to undergo chain transfer and chain termination reactions. In other words, systems suitable for inducing a fast interconversion between the dormant and the reactive radical species having a high electron density at the radical center derived from NVC were difficult to find. However, recent advances in the field of controlled radical polymerization have resulted in successful controlled polymerization of NVC.

Despite apparent difficulty of controlled radical polymerization of nonconjugated *N*-vinyl monomers, several



Scheme 4. Structures of dithiocarbamate, dithioester, and trithiocarbonate-type chain transfer agents (CTAs) used for RAFT polymerization of nonconjugated *N*-vinyl monomers.

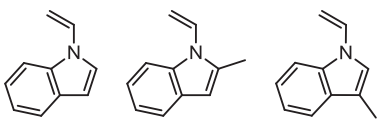
attempts to synthesize poly(NVC) using controlled radical polymerization systems have been reported in the literature. Initially, Fukuda et al. demonstrated that the control of NVC homopolymerization could not be achieved by a typical NMP, whereas the copolymerization with St under the same conditions proceeded in a living fashion [46]. Shmidt-Naake et al. also reported the controlled NMP of St and NVC, while they demonstrated that the synthesis of the homopolymer, poly(NVC), with controlled molecular weights and a narrow polydispersity, was still problematic [47,48]. Nowakowska et al. reported that the synthesis of poly(sodium styrenesulfonate-*b*-NVC) by NMP was possible only when the polymerization of NVC was conducted in the presence of acetic anhydride as an accelerator [49]. ATRP ($C_{60}Cl_n$/CuCl/2,2′-bipyridine) was also used for the synthesis of poly(NVC) having a narrow polydispersity (M_w/M_n = 1.33) [50]. However, the actual structure of the product was a star-like architecture with a C_{60} core because of multiple chlorine atoms in one initiator molecule, $C_{60}Cl_n$, and there was no information on each poly(NVC) and its detachments from the surface of C_{60}. They also demonstrated that the attempt to synthesize the block copolymer, poly(NVC-*b*-St), using the ATRP system provided products with bimodal molecular weight distributions [51]. These previous studies failed to provide convincing proof of the controlled character of the

homopolymerization of NVC, such as a kinetic investigation, evaluation of the end groups, and a chain extension experiment.

In 2006, we reported the synthesis of poly(NVC) with predetermined molecular weights (M_n in the range of 3000–48,000) and low polydispersities (M_w/M_n in the range of 1.15–1.20) by xanthate-mediated controlled radical polymerization using a xanthate-type CTA having a —$CH(CH_3)$Ph moiety as a leaving group (**CTA 2**) [52]. Good control of the polymerization of NVC was confirmed by the linear first-order kinetic plot, the molecular weight controlled by the monomer/CTA molar ratio, linear increase in the molecular weight with the conversion, and the ability to extend the chains by the second addition of the monomer. The investigations with various xanthate-type CTAs (**CTA 1, CTA 2,** and **CTA 4**) suggested the effectiveness of the leaving group structures (R = $CH(CH_3)$Ph and $CH(CH_3)COOCH_3$ in S = C(OEt)S-R; **CTA 2** and **CTA 4**) in the xanthate derivatives for the controlled polymerization of NVC [52,53]. In contrast, the polymerization of NVC with dithiocarbamate-type (**CTA 21**) or dithioester-type (**CTA 35**) mediating agents exhibited the inhibition the polymerization or the formation of the products with broad molecular weights distributions.

The xanthate-mediated controlled radical polymerization of NVC was then extended to the *N*-vinylindole (NVIn) derivatives [54]. The controlled radical polymerization of three *N*-vinylindole derivatives, *N*-vinylindole (NVIn), 2-methyl-*N*-vinylindole (2MNVIn), and 3-methyl-*N*-vinylindole (3MNVIn), were investigated by RAFT/MADIX process (Scheme 5). Although the stabilizing effect of NVIn ($Q = 0.53$, $e = -1.30$) is slightly higher than that of NVC ($Q = 0.26$, $e = -1.29$) with a similar electron-donating property, NVIn has been reported to have a lower activation energy ($E_A = 17.5$ kJ/mol^{-1}) than that of NVC (27.4 kJ/mol), suggesting that the propagating NVIn radical possesses higher reactivity [55]. Among various CTAs (**CTAs 1-2**, **CTA 12**, **CTA 21**, and **CTA 35**), the xanthate-type RAFT agent (**CTA 2**) was the most efficient for obtaining poly(2MNVIn) with controlled molecular weights ($M_n = 1{,}700$–$19{,}400$) and narrow molecular weight distributions ($M_w/M_n = 1.20$–1.40).

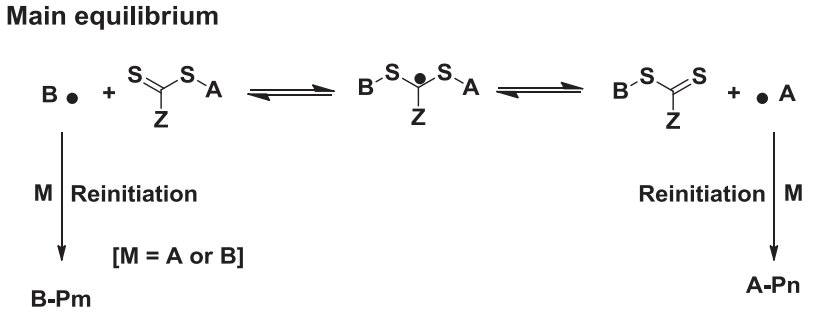
In the past few decades, considerable attention has been given to the block copolymers having poly(NVC) segment, mainly as a result of the feasibility to create highly ordered structures and their potential applications in the optoelectronic fields. Depending on the ordered structures and stacking of the carbazole moiety, the three-dimensional hierarchical structures formed by self-organization of the carbazole-containing block copolymers may lead to unique electronic and photonic functions. Multiscale ordering of such functional nanomaterials is a powerful technique for the creation of novel polymeric materials for optoelectronic applications. Regardless of the potentially interesting properties of the resulting products, the synthesis of well-defined block copolymer derived from *N*-vinyl monomers was challenging, owing to the low reactivity of nonconjugated *N*-vinyl monomers and the low stability of the propagating radicals. For the synthesis of well-defined block copolymers by the RAFT process, the blocking order is crucial. The first dithioester-terminated polymer, S=C(Z)S-A, in which the A block corresponds to the first polymer and Z is the stabilizing group, should have a high transfer constant in the subsequent polymerization of the second monomers to give the B block, as shown inScheme 6 [56,57]. The rapid conversion of macro-CTA to a block copolymer is also required to achieve a block copolymer with low polydispersity, which allows all the second blocks to be initiated at approximately the same time [58,59].



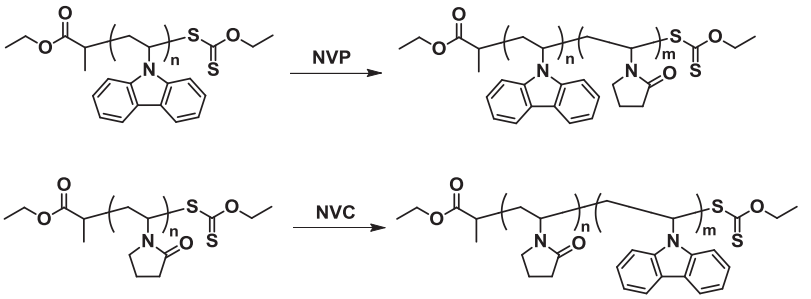
Scheme 5. Structures of *N*-vinylindole derivatives.

The xanthate-mediated controlled radical polymerization of NVC has been successfully applied for the synthesis of a variety of well-defined block copolymers involving a poly(NVC) segment. For example, amphiphilic block copolymers, poly(NVC)-*b*-poly(NVP), were prepared by xanthate-mediated RAFT polymerization of two nonconjugated *N*-vinyl monomers (Scheme 7) [60]. Both poly(NVC) and poly(NVP) prepared using **CTA 5** and the resulting block copolymers had molecular weights close to theoretical values in the range of $M_n = 30{,}000$–$90{,}000$ with relatively low polydispersities (M_w/M_n in the range of 1.28–1.51). The amphiphilic block copolymers dissolved in several organic solvents; however, depending on their composition, they formed either micelles or large aggregates in methanol. The xanthate-mediated RAFT polymerization of NVC was applied for the synthesis of three types of block copolymers, poly(ethylene glycol)-*b*-poly(NVC), poly(NVC)-*b*-poly(VAc), and poly(NVC)-*b*-poly(vinyl alcohol), as shown in Scheme 8 [61]. A series of poly(ethylene glycol)-*b*-poly(NVC) with a wide range of poly(NVC) chain lengths ($M_n = 9800$–$55{,}400$, $M_w/M_n = 1.06$–1.29) was obtained using poly(ethylene glycol) macro-CTA (**CTA 15**). The synthesis of well-defined block copolymer based on NVC and VAc, which can be regarded as nonconjugated *N*-vinyl and *O*-vinyl monomers, needed to consider the polymerization sequence, even if both monomers could be homopolymerized in a controlled fashion by RAFT polymerization with the same RAFT agent (**CTA 5**). In this system, well-defined block copolymers ($M_n = 5600$–$10{,}100$, $M_w/M_n = 1.35$-1.52) were obtained only by RAFT polymerization of VAc using poly(NVC) macro-CTA. A well-defined block copolymer involving a poly(lithium vinyl sulfonate) segment was synthesized by RAFT polymerization of a vinyl sulfonate ester, neopentyl ethenesulfonate, using xanthate-terminated poly(NVC) macro-CTA prepared with **CTA 4**, followed by deprotection (Scheme 9) [62]. The resulting product can be regarded as an amphiphilic block copolymer, comprising poly(lithium vinyl sulfonate) as a strong anionic polyelectrolyte and poly(NVC) as a hydrophobic segment.

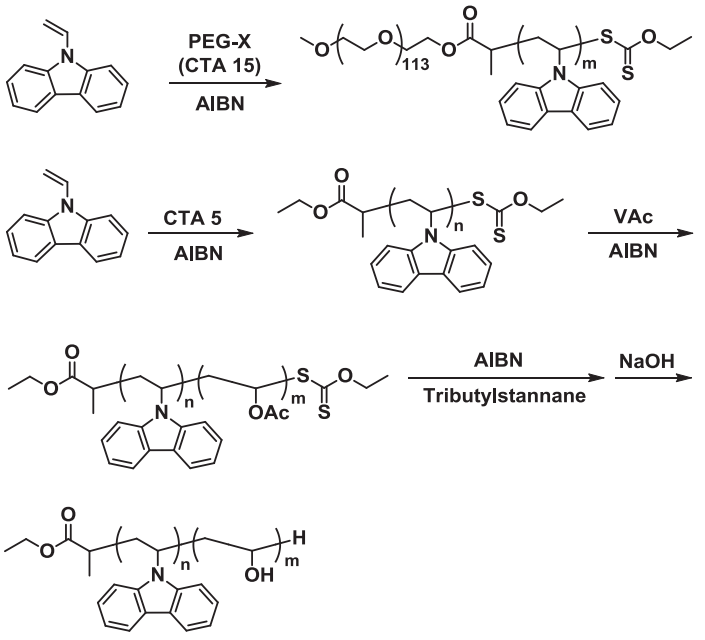
Generally, the selection of the RAFT agent is dictated by the types of monomer being polymerized. The RAFT agents (dithioesters, trithiocarbonates) suitable for controlling



Scheme 6. Mechanism of RAFT polymerization for the synthesis of a block copolymer; A and B are different monomers.

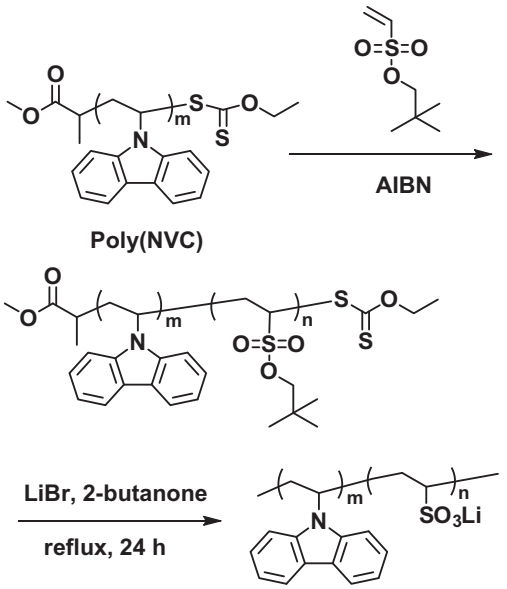


Scheme 7. Synthesis of poly(NVC)-*b*-poly(NVP)s by xanthate-mediated RAFT polymerization.



Scheme 8. Synthesis of poly(ethylene glycol)-*b*-poly(NVC), poly(NVC)-*b*-poly(VAc), and poly(NVC)-*b*-poly(vinyl alcohol) by xanthate-mediated RAFT polymerization.

polymerization of "more activated" monomers (e.g., St, acrylates, and methacrylates) tend to inhibit polymerization of "less activated" monomers (e.g., NVC, VAc, and NVP). Similarly, RAFT agents suitable for polymerizations of "less activated" monomers tend to give little or poor control over polymerizations of "more activated" monomers. Hence, the synthesis of block copolymers composed of "less activated" and "more activated" monomers was difficult. Recently, switchable RAFT polymerization using *N*-(4-pyridinyl)-*N*-methyldithiocarbamates (**CTAs 22–24**)



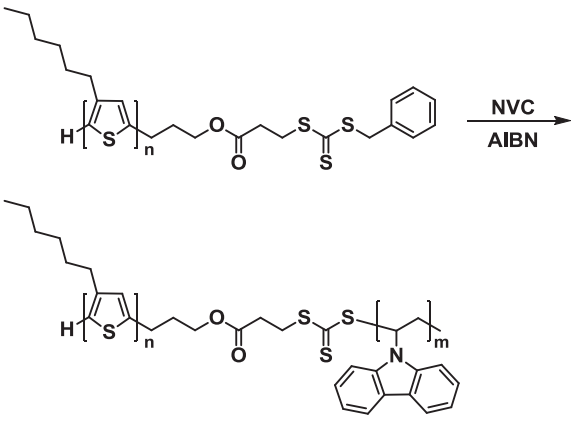
Scheme 9. Synthesis of poly(NVC)-*b*-poly(lithium vinyl sulfonate) by RAFT polymerization of neopentyl ethenesulfonate using poly(NVC) as macro-CTA and subsequent deprotection.

was found to provide excellent control over polymerization of "less activated" monomers and, after addition of 1 equiv of a protic or Lewis acid (CTA 26), become effective in controlling polymerization of "more activated" monomers [63]. Switchable RAFT polymerization allowed the synthesis of poly(methyl acrylate)-*b*-poly(NVC) with narrow molecular weight distributions (M_n = 48,000, M_w/M_n = 1.33). The preparation of unimodal low dispersity poly(*N*,*N*-dimethylacrylamide)s was also conducted by aqueous RAFT polymerization using switchable RAFT agents (**CTA 22**, **CTA 24**, and **CTA 25**), and block copolymer of poly(*N*,*N*-dimethylacrylamide) with poly(NVC) (M_n = 16,400, M_w/M_n = 1.13) was achieved using**CTA 22** [64]. Acid/base switchable *N*-aryl-*N*-pyridyl dithiocarbamates (**CTAs 22, 27-31**), which vary in substituent at the 4-position of the aryl ring, were employed for the study of chain transfer kinetics in polymerization of conjugated and nonconjugated monomers, including NVC [65]. The kinetic study demonstrated the influence of polar effects on the apparent chain transfer coefficient and supported the hypothesis that the activity of these RAFT agents is determined by the availability of the lone pair of the dithiocarbamate nitrogen. The controlled radical polymerizations of "less activated" monomers, NVC, VAc, and NVP, were successfully achieved in the presence of a disulfide, isopropylxanthic disulfide, using AIBN as the initiator [66]. The polymerization proceeded via RAFT/MADIX process, where xanthate was formed in situ from the reaction of AIBN and isopropylxanthic disulfide.

The synthesis of poly(NVC)-based block copolymers functionalized with rhenium diimine complexes or pendant terpyridine ligands was reported [67]. The block copolymers were synthesized by RAFT polymerization of methacrylate derivatives having functional side chains using poly(NVC) macro-CTA prepared with the xanthate-type CTA (**CTA 2**). The products exhibited interesting morphological properties as a result of the phase separation between different blocks. It was demonstrated that the rhenium complex polymer block could function as a photosensitizer, while the terpyridine-containing polymer block could be used as a template for nanofabrication by selective deposition of zinc complexes.

In some cases, trithiocarbonate-type CTAs were employed for poly(NVC)-containing block copolymers. Thermo- and pH-multi-responsive fluorescent micelles based on the self-assembly of diblock copolymers, poly(NIPAAm-*co*-NVC)-*b*-poly[2-(dimethylamino)ethylacrylate], were obtained by RAFT copolymerization of *N*-isopropylacrylamide (NIPAAm) and NVC, followed by chain extension in the presence of 2-(dimethylamino)ethyl acrylate) [68]. When the polymerization was carried out with trithiocarbonate-type CTA (**CTA 40**), the resulting block copolymer exhibited low polydispersity (M_n = 52,400, M_w/M_n = 1.20). The presence of NVC in concentrations as low as 4% in the core of the micelles was reported to allow the nanoparticles to be tagged by fluorescence, making them well suited to therapeutic applications. Very recently, Keddie and Moad reported that controlled character of the RAFT polymerization of NVC was achieved using trithiocarbonates [69]. They demonstrated that NVC has intermediate reactivity, i.e. between that of the traditional more activated and less activated monomers, and a further key to good control is the selection of RAFT agent R substituent group to be both a good leaving group and a good initiating radical. Among various CTAs (**CTA 2**, **CTA 11**, **CTA 22, CTA 30**, **CTA 37, CTA 41**, and **CTAs 45–46**), a trithiocarbonate with cyanomethyl R group (**CTA 45**), which meets the criteria, was the most efficient for obtaining poly(NVC) with narrow molecular weight distributions (M_w/M_n < 1.1). Well-defined block copolymers, poly(*n*-butyl acrylate)-*b*-poly(NVC) and poly(St)-*b*-poly(NVC), were obtained using the trithiocarbonate RAFT agent (**CTA 45**).

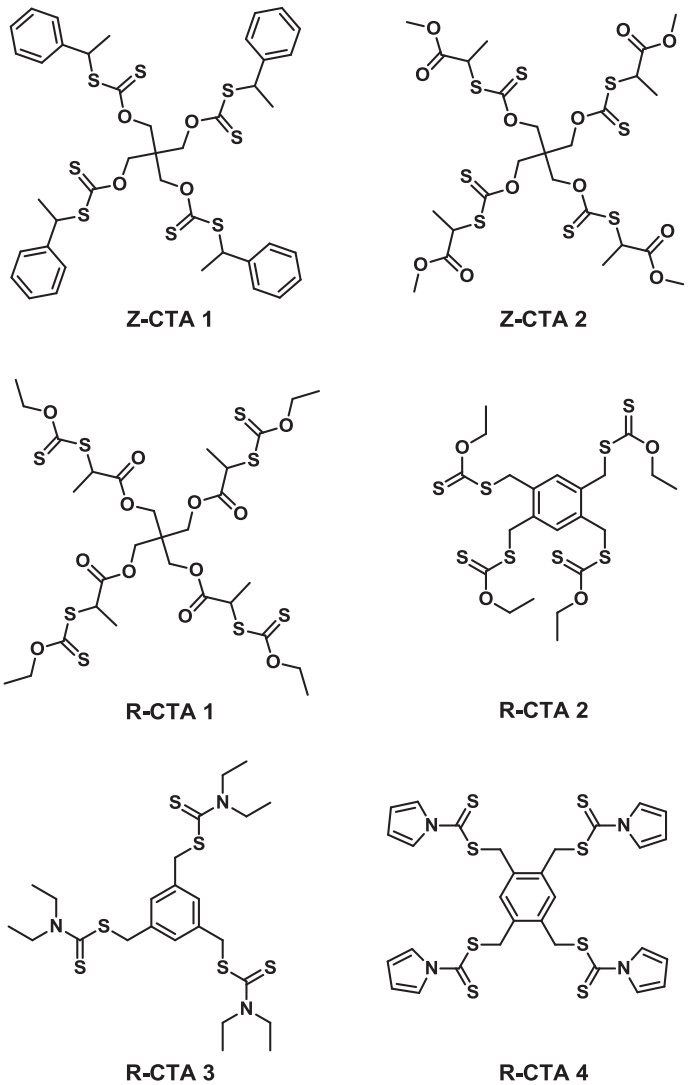
A rod-coil block copolymer consisting of poly(3-hexylthiophene) and poly(NVC) was synthesized by RAFT polymerization of NVC using trichiocarbonate-terminated poly(3-hexylthiophene) as a macro-CTA (Scheme 10)



Scheme 10. Synthesis of poly(3-hexylthiophene)-*b*-poly(NVC) by RAFT polymerization.

[70]. Using the living Grignard metathesis and end-capping method, followed by the transformation of the end-group, hydroxypropyl-terminated poly(3-hexylthiophene) was obtained, which in turn was converted to the trichiocarbonate-terminated macro-CTA. The rod-coil block copolymer (M_n = 13,800, M_w/M_n = 1.51) was obtained, which was employed for a white organic electroluminescence device. It was possible to suppress energy transfer from poly(NVC) as wide bandgap units to poly(3-hexylthiophene) as low bandgap blocks by obtaining the phase separated domains from thin films of the resulting block copolymer, yielding dual emissions for white electroluminescence with ICE (Commission Internationale de l'Éclairage) coordination of (0.34, 0.33).

In addition to RAFT/MADIX process, other controlled radical polymerizations, involving ATRP, SET-LRP, organoheteroatom-mediated living radical polymerization, have been recently recognized as useful systems to achieving controlled polymerization of NVC. The homopolymerization of NVC via ATRP was investigated with Cu(I)/Cu(II)/2,2′-bipyridine as the catalyst system at 90 °C in toluene [71]. *N*-2-Bromoethyl carbazole was used as the initiator, and the optimized ratio of Cu(I) to Cu(II) was found to be 1/0.3. The resulting poly(NVC) was used as a macroinitiator for the ATRP of methyl methacrylate (MMA), and this resulted in the formation of a block copolymer (M_n = 4600, M_w/M_n = 1.30). The order of blocking is considered to be also crucial for ATRP or NMP as RAFT process. The polymerization of NVC was compared with various controlled radical polymerization methods, such as ATRP, SET-LRP, and single electron transfer initiation followed by RAFT (SET-RAFT)[72]. In the case of NVC, well-controlled polymerization with narrow molecular weight distribution was achieved by high-temperature ATRP, while SET-RAFT polymerization was relatively slow and controlled at ambient temperature. The synthesis of diblock copolymers was



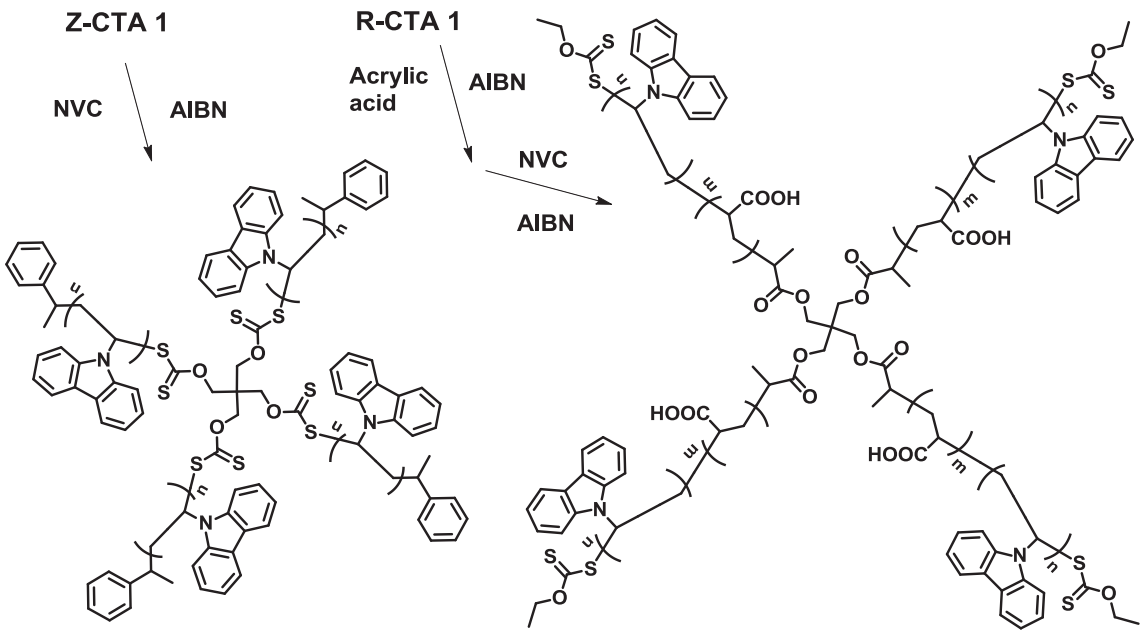
Scheme 11. Structures of R- and Z-designed tetrafunctional CTAs.

achieved from poly(NVC) macroinitiator using a flavanone-based methacrylate as the second monomer. Organoheteroatom-mediated living radical polymerization using organotellurium, organostibine, and organobismuthine chain transfer agents were also useful methods for achieving the controlled polymerization of conjugated and nonconjugated monomers [28]. For example, organotellurium-mediated radical polymerization of NVC under UV–vis irradiation led to the formation of highly controlled living polymer with predetermined molecular weights and narrow molecular weight distribution (M_n = 21,200, M_w/M_n = 1.11) [73].

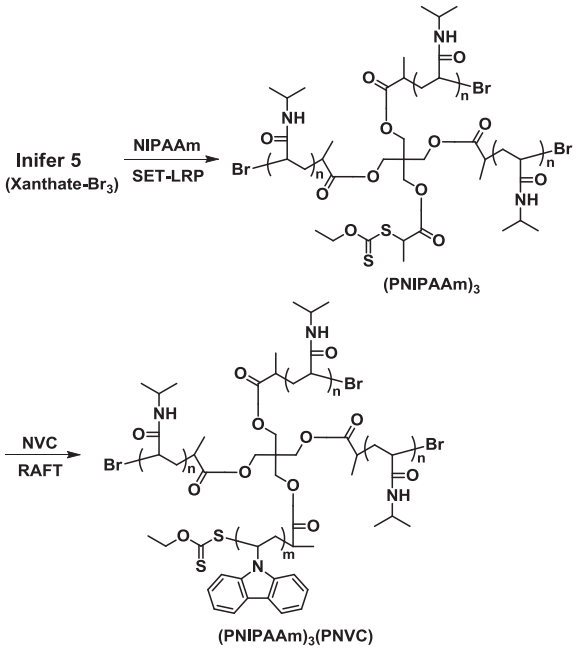
The design and synthesis of novel star copolymers having characteristic architectures, such as star block copolymers and heteroarm or miktoarm (mixed) star polymers, have attracted significant research interest because of their interesting structures and properties [74–80]. Amphiphilic star block copolymers and miktoarm star polymers can form a variety of superstructures as a result of self-organization, and the resulting assembled structures should be governed by the branched architecture, as well as the chemical nature of the components, their composition, and molecular weight. There are two basic routes for synthesizing star polymers [81]; the "core first" method (polymerization from multifunctional initiators or microgels), and the "arm first" method, in which growing polymer chain ends are reacted with a multifunctional terminating agent or a divinyl compound. In the RAFT/MADIX system, two different approaches can be used for the synthesis of star polymers; the so-called R-group approach (propagation attached to core) and Z-group approach (propagation away from core) [18,82–86]. A variety of multifunctional CTAs were developed for the controlled synthesis of star polymers derived from N-vinyl monomers (Scheme 11).

The xanthate-mediated RAFT polymerization of NVC using Z-designed tetrafunctional CTA (**Z-CTA 1**) was initially applied for the synthesis of poly(NVC) star polymers (Scheme 12) [87]. Later, RAFT polymerization of NVC was investigated using three different xanthate-type tetrafunctional CTAs: two Z-designed CTAs having different R (leaving) groups (**Z-CTA 1** and **Z-CTA 2**) in which the Z (stabilizing) groups are linked to the core, and one R-designed CTA (**R-CTA 1**). The R-group approach was found to be the most efficient for the controlled synthesis of four-arm poly(NVC) stars having low polydispersities and controlled molecular weights (M_n = 33,300–102300, M_w/M_n = 1.14–1.38). Amphiphilic star block copolymers having low polydispersities (M_w/M_n = 1.22–1.33) were synthesized by the polymerization of NVC using the poly(acrylic acid) star, which was prepared from the R-designed tetrafunctional CTA (**R-CTA 1**), as shown in Scheme 12 [53]. The formations of the micelles and inverse micelles were observed in water, which is a good solvent only for the poly(acrylic acid) segment, and in $CHCl_3$, which is a good solvent only for poly(NVC) segment. The absorbance and fluorescence spectra indicated that specific conformations of amphiphilic stars, like micelles and inverse micelles, affected the characteristic optoelectronic properties.

Synthesis of poly(NVC) star by microwave-assisted RAFT polymerization was also conducted using R-designed CTA (**R-CTA 3**) containing a 1.3.5-trisubstituted benzene ring as core and three dithiocarbamate functionalities attached through an intermediate for fragmenting covalent bonds. The resulting products exhibited a trimodal distribution, assigned to the linear and star–star coupling polymers, accompanying the real star polymer (as main product) [88]. The structure of *N*,*N*-diethyldithiocarbamate moiety was the same to that used for so-called



Scheme 12. Synthesis of poly(NVC) star and amphiphilic star block copolymers.



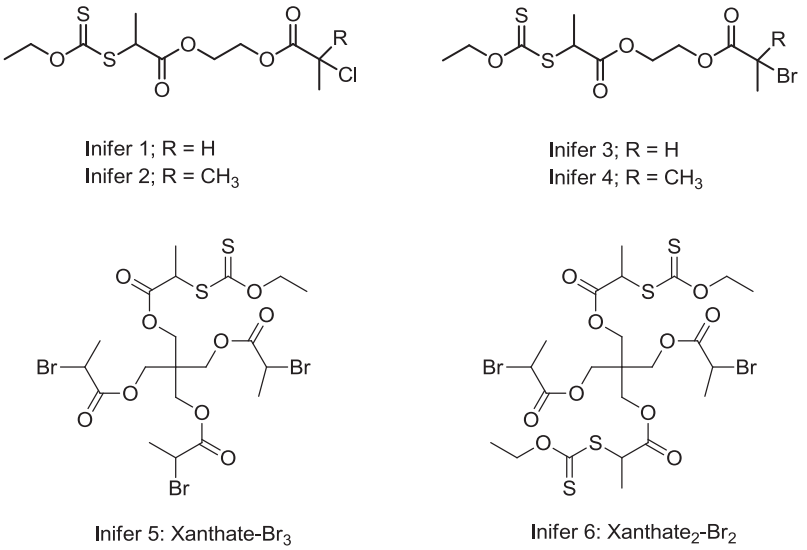
Scheme 13. Synthesis of A_3B miktoarm star copolymer, poly(NIPAAm)$_3$-poly(NVC).

photoiniferter system (photoinitiator–transfer agent–terminator) [89].

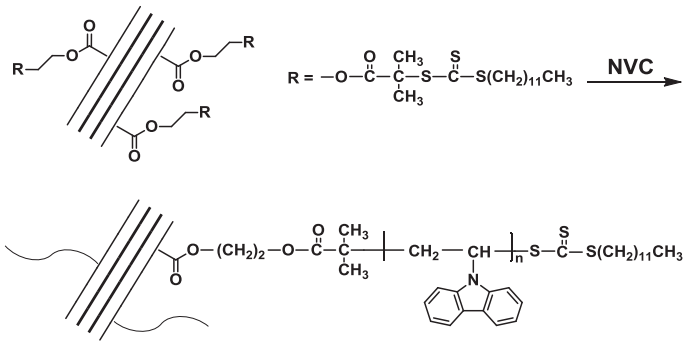
Star polymers containing chemically different arms are designated heteroarm or miktoarm (mixed arm) star polymers when they comprise two or more different kinds of arms, respectively. Their unique architectures cause them to reveal interesting properties in the solid state and in solution [90]. An amphiphilic A_3B miktoarm star copolymer, poly(NIPAAm)$_3$-poly(NVC), was successfully synthesized by a combination of SET-LRP and RAFT polymerization (Scheme 13) [91]. First, the well-defined three-armed poly(NIPAAm) was prepared via SET-LRP of NIPAAm using a tetrafunctional bromoxanthate inifer (**Inifer 5**; xanthate-Br$_3$, Scheme 14) as the initiator and Cu(0)/PMDETA as a catalyst system. Secondly, the target amphiphilic A_3B miktoarm star copolymer was prepared via RAFT polymerization of NVC employing three-armed poly(NIPAAm) having a xanthate moiety as the macro-CTA. The amphiphilic A_3B miktoarm star copolymer showed an increase in the fluorescence intensity of micelle with temperature and had good temperature reversibility.

In recent years, much interest has been devoted to the design and synthesis of carbazole-containing polymer chains attached to planar and spherical surfaces as candidates for various optoelectronic industrial applications. Poly(NVC) grafted on electroactive substrates, such as carbon nanotubes, fullerene, graphene, and quantum dots, has been extensively investigated, owing to many scientific and industrial applications. The so-called "grafting onto," and "grafting from" methods can be used for the synthesis of carbazole-containing hybrids. In the "grafting from" process, the side chains of the brush are formed via controlled radical polymerizations involving ATRP and NMP initiated by the pendant initiating groups on the surface. When RAFT polymerization was employed, the CTA moiety was attached to the surface. Well-defined polymer brushes with high grafting density and rather narrow distributions can be obtained using this method [92–94]. The "grafting onto" technique was frequently used for the synthesis of the hybrids, in which the carbazole-containing polymers were attached to the substrates by adsorption or chemical reaction of end-functionalized polymers or block copolymers onto the surfaces.

The poly(NVC)-grafted multiwalled carbon nanotubes hybrid materials were synthesized by RAFT polymerization of NVC in the presence of a trithiocarbonate-type CTA functionalized covalently onto multiwalled carbon nanotubes (Scheme 15) [95]. The poly(NVC) removed from the multiwalled carbon nanotubes in the presence of 3-chloroper-



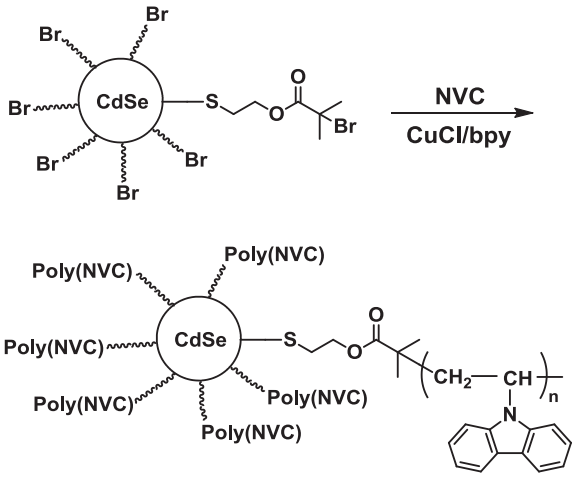
Scheme 14. Structures of haloxanthate inifers and tetrafunctional bromoxanthate inifers.



Scheme 15. Synthesis of poly(NVC)-grafted multiwalled carbon nanotubes by RAFT polymerization of NVC.

oxybenzoic acid had broad molecular weight distributions (PDI = 1.62–1.71) due to the steric hindrance effect and different numbers of CTA groups onto the surface. Incorporation of poly(NVC) onto the surfaces of the multiwalled carbon nanotubes can considerably improve their solubility and processability. Hybrid materials that are suitable candidates for viable optical limiting devices exhibit significant nonlinear optical responses. Poly(NVC) chemically modified graphene oxide was obtained by RAFT polymerization of a trithiocarbonate type-CTA functionalized on graphene oxide [96,97]. The poly(NVC) covalently grafted onto graphene oxide has M_n of 8050 and a polydispersity of 1.43 [97]. The resulting hybrid material showed good solubility in organic solvents and a significant energy bandgap in the vicinity of 2.49 eV. The poly(NVC)-C_{60} composites were synthesized by ATRP ($C_{60}Cl_n$/CuCl/2,2′-bipyridine) of NVC [50,98,99]. The photoconducting properties of poly(NVC)-C_{60} composites were also investigated.

The CdSe-polymer composite was prepared via ATRP of NVC on functionalized CdSe quantum dots (Scheme 16) [100,101]. The poly(NVC) chains grafted onto the CdSe surface had low molecular weights (M_n < 1500) and low polydispersities (M_w/M_n < 1.2). It was revealed that grafting poly(NVC) onto the surface of CdSe nanocrystals would reduce the bandgap of poly(NVC) and cause a red shift in the emission peak. The nanocrystal–polymer nanocomposite was employed as the electron acceptor in polymer bulk heterojunction solar cells. Ultrasound-assisted bulk synthesis of CdS-poly(NVC) nanocomposites was reported via RAFT polymerization [102]. The poly(NVC) removed from the CdS nanoparticle under the acidic condition had a broad molecular weight distributions (PDI = 3.6).



Scheme 16. Synthesis of CdSe-polymer composite by ATRP of NVC.

Polymer brushes refer to an assembly of polymer chains, which are tethered by one end to a surface or an interface. Surface-initiated polymerization has the advantage of allowing easy modification of surface properties by varying the composition of the polymer brush, grafting density, and the degree of polymerization [92–94]. Electrochemically crosslinked surface-grafted poly(NVC) brushes have been demonstrated as hole transport layers on a photovoltaic device using surface-initiated polymerization [103,104]. The surface bound free radical initiator was used for the modification of ITO substrate. The pendant carbazole group made the poly(NVC) an electrochemically cross-linkable precursor, capable of forming conjugated polymer network films. The covalent linkage of the poly(NVC) brush allowed for direct electroluminescent device preparation on modified ITO, giving the advantage of strong adhesion to ITO with possible long-term stability against acid dopants and oxygen.

3. *N*-vinyl pyrrolidone (NVP), *N*-vinylcaprolactam (NVCL), and noncyclic *N*-vinyl amides

N-vinyl pyrrolidone (NVP) is a representative nonconjugated *N*-vinyl monomer, which affords an important water-soluble polymer by conventional radical polymerization. Poly(NVP) has been utilized in a variety of applications, particularly in biomedical fields and in the cosmetic industry, because of many desirable properties including low toxicity, chemical stability, and good biocompatibility. Recently, controlled radical polymerization of NVP has received increasing attention, as it offers the possibility to produced functional polymers having various architectures, such as block and graft copolymers, star and branched polymers, and hybrids, as shown below. The controlled radical polymerization of NVP was introduced as one section in two recent reviews [15,105].

RAFT polymerization is one of the most useful approaches to attain controlled character of the polymerization of NVP. Among various CTAs, dithiocarbonates (xanthates) and dithiocarbamates were frequently employed for controlling the radical polymerization of NVP. In their review, Moad et al. described RAFT polymerization of NVP using a xanthate-type CTA (**CTA 11**), affording a poly(NVP) with a relatively low polydispersity (M_w/M_n = 1.35) [10]. Devasia et al. reported controlled radical polymerization of NVP using a dithiocarbamate-type CTA (**CTA 32**) in the presence of AIBN [106]. The controlled nature of the polymerization was confirmed by pseudo-first order kinetics, a linear increase in the molecular weights with conversion, end-group analysis, and chain extension experiment. Diblock copolymers (M_w/M_n = 1.23–1.44) were obtained by sequential addition of monomers such as St or *n*-butyl acrylate using the poly(NVP) macro-CTA prepared with **CTA 32**. Wan et al. reported controlled radical polymerization of NVP using xanthate-type CTAs in fluoroalcohols for simultaneous control of molecular weight and tacticity [107]. They demonstrated that xanthate-type CTAs (**CTA 1** and **CTA 2**) showed good control of the polymerization of NVP after the induction period, while a dithioester-type CTA (**CTA 38**) inhibited the polymerization. Subsequent studies of RAFT polymerization of NVP using various CTAs (**CTA 5**, **CTAs 9–10**, and **CTAs 12–14**) indicated that the selection of the xanthate-type CTAs was crucial to obtain well-defined poly(NVP)s with significant effect of the leaving (R) group on the controlled character [108,109]. Pound et al. also reported that several unexpected by-products were formed during the RAFT/MADIX polymerization of NVP using *O*-ethyl xanthates. Postma et al. reported that the polymerization of NVP in the presence of phthalimidomethyl xanthate (**CTA 19**) provided good control without inhibition period, whereas the polymerization of phthalimidomethyl trithiocarbonate (**CTA 39**) was characterized by induction period [110]. RAFT polymerization of NVP using prop-2-ynyl morpholine-4-carbodithioate (**CTA 33**) was also reported [111]. The RAFT/MADIX polymerization of NVP was successfully carried out in homogeneous water medium at low temperature (25 °C) using xanthate-type **CTA 4** with the *tert*-butyl hydroperoxide/ascorbic acid redox initiator [112]. It was demonstrated that the known by-products due to the hydrolysis or coupling of NVP were absent under the conditions, and xanthate moiety was attached to the polymer backbone. The switchable RAFT agent (**CTA 24**) was found to provide poly(NVP) with a low polydispersity (M_w/M_n = 1.19) in the absence of acid [63].

Bilalis et al. reported controlled NMP and RAFT polymerization of NVP and the synthesis of block copolymers [113]. 2,2,6,6-Tetramethyl-1-(phenyl-ethoxy)piperidine and AIBN/TEMPO were employed for NMP of NVP in the presence of acetic anhydride acted as an accelerator, giving poly(NVP)s with relatively high polydispersities ($M_w/M_n \geqq 1.7$). They also investigated RAFT polymerization of NVP using dithioester- and trichiocarbonate-type CTAs (**CTA 36**, **CTA 41**, and **CTA 42**), and demonstarated that the poly(NVP)s with relatively low polydispersities ($M_w/M_n \approx 1.5$) were obtained using **CTA 41** under suitable conditions. The controlled character of the NVP polymerization was manifested by the efficient synthesis of block copolymers.

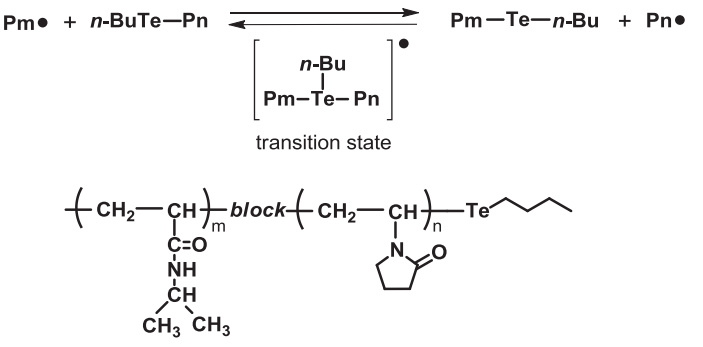
Poly(NVP)s with well-defined macromolecular structure were prepared by oganostibine [114,115], organotellurium [116], and organobismuthines [117] mediators, and organotellurium irradiated by UV–vis light [73]. The cobalt-mediated radical polymerization of NVP was investigated with various bis(acetylacetonate)cobalt(II) derivatives, which afforded poly(NVP) with relatively broad polydispersities (1.7–2.0) [118]. They reported that better control over M_n and polydispersity in the polymerization of NVP was achieved by addition of VAc to the reaction, and statistical copolymerization proceeded in a controlled manner. The cobalt-mediated radical polymerization of NVP was extended for the synthesis of block copolymers, as shown later [119]. At room temperature ATRP of NVP was carried out with methyl 2-chloropropionate and copper(I) chloride used as initiator and catalyst in the presence of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (Me_6Cyclam) as ligand [120]. In the system, the polymerization of NVP via ATRP could be mediated by the addition of $CuCl_2$, giving poly(NVP)s with controlled M_n values up to 8900 and relatively low polydispersities (M_w/M_n = 1.2–1.3).

A variety of block copolymers having poly(NVP) segment were synthesized by RAFT chain extension approach. In 2006, Nguyen et al. reported that poly(NVP)s prepared by RAFT polymerization of NVP with xanthate-type CTAs (**CTA 1** and **CTA 2**) were employed for the chain extension with VAc, which resulted in the formation of poly(NVP)-*b*-poly(VAc) block copolymers (M_w/M_n = 1.45–1.55) [121]. The prepared block copolymers were used as stabilizers in suspension polymerization. Xanthate-type CTA having carboxylic acid moiety (**CTA 9)** was also employed for the synthesis of the amphiphilic block copolymers consisting of NVP and VAc via RAFT/MADIX polymerization [122]. The resulting block copolymers obtained at different comonomer compositions in the feed had relatively broad molecular weight distributions (M_w/M_n = 1.58–2.23). Poly(NVP)-*b*-poly(VAc) block copolymers of varying molar mass and hydrophobic block lengths were also synthesized by xanthate-mediated radical polymerization using **CTA 12** [123]. The amphiphilic block copolymers (M_w/M_n = 1.6–1.7) having different poly(NVP) contents employed as drug delivery vehicles for hydrophobic drugs [124]. Pound et al. reported xanthate-mediated copolymerization of NVP for the synthesis of double-hydrophilic block copolymers with poly(ethylene glycol), in which the leaving group of the macro-CTAs played a crucial role in the preparation of the block copolymers [125]. Block copolymers were obtained when the macro-CTA had a propionyl ester leaving group (**CTA 15** and **CTA 17**), whereas under the same experimental conditions the macro-CTA with a phenylacetyl ester leaving group (**CTA 16**) inhibited the polymerization. Poly(ethylene glycol)-*b*-poly(NVP) and poly(NVP)-*b*-poly(ethylene glycol)-*b*-poly(NVP) were obtained with very low polydispersities (PDI $\sim$ 1.1), when the poly(NVP) segments were short ($M_n \sim 5000$). With a longer poly(NVP) segment ($M_n \sim 39{,}000$), an increase in polydispersity was observed (PDI $\sim$ 1.4). The switchable RAFT agent (**CTA 22**) was also applied for the block copolymer, poly(*N*,*N*-dimethylacryla-

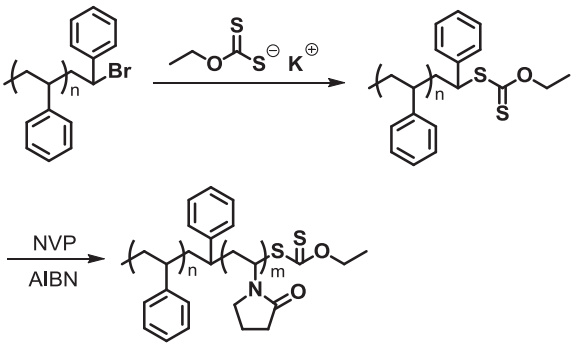
mide)-*b*-poly(NVP) (M_n = 16,000, M_w/M_n = 1.19) [64]. Double-hydrophilic block copolymers, poly(acrylamide)-*b*-poly(NVP) (M_n = 8600–12,200, M_w/M_n = 1.09–1.25), were obtained by RAFT/MADIX polymerization of NVP in water 25 °C using xanthate-terminated poly(acrylamide) macro-CTAs prepared with **CTA 4** [112].

As mentioned above, RAFT chain extension was an useful approach to synthesize block copolymers composed of two nonconjugated monomers (“less activated” monomers), whereas the synthesis of block copolymers composed of “less activated” and “more activated” monomers was difficult. Nevertheless, various block copolymers were synthesized by sequential RAFT polymerization of nonconjugated NVP (“less activated” monomer) and conjugated monomers (“more activated” monomers). For example, poly(NVP)-*b*-poly(St) diblock copolymer was synthesized via sequential RAFT polymerization of NVP using poly(St) macro-CTA prepared with **CTA 2** as a xanthate-type CTA [126]. Since the xanthate-type CTA is not suitable mediating agent for the controlled polymerization of St, the resulting block copolymers showed relatively high polydispersities (M_w/M_n > 1.5). The block copolymer was incorporated into polybenzoxazine to access the nanostructures in the thermosets. The amphiphilic triblock copolymers of poly(NVP)-*b*-poly(MMA)-*b*-poly(NVP) were synthesized via RAFT polymerization using a trithiocarbonate (**CTA 42**) [127]. The resulting block copolymers showed relatively high polydispersities (M_w/M_n = 1.40–1.69), which is mainly due to the usage of ineffective trithiocarbonate mediating agent for the controlled radical polymerization of NVP. Using these copolymers as additives in casting solutions, the porous blend membranes of poly(vinylidene fluoride) and the triblock copolymers were prepared following a typical nonsolvent induced phase separation process. Similarly, amphiphilic triblock copolymer of poly(NVP)-*b*-poly(MMA)-*b*-poly(NVP) synthesized via RAFT polymerization with **CTA 42** was directly blended with polyethersulfone using dimethylacetamide as the solvent to prepare flat sheet and hollow fiber membranes using a liquid–liquid phase separation technique [128]. Hu and Zhang reported the synthesis of gradient polymer by complex-radical terpolymerization of St, maleic anhydride, and NVP via γ-ray irradiation by use of a RAFT process with a trithiocarbonate-type CTA (**CTA 43**) [129]. The terpolymerization proceeded mainly through “complex” mechanisms in the state of near-binary copolymerization of St-maleic anhydride and maleic anhydride-NVP charge-transfer complexes. The significant difference in the value of the reactivity ratios between the two complexes led to the formation of the “gradient” ABA-type block copolymers (M_w/M_n = 1.17–1.47), in which more St-maleic anhydride complex is located in the middle of the polymer, whereas maleic anhydride-NVP complex is existed at the both ends of the polymer. The gradient copolymers synthesized by RAFT polymerization were employed as dispersion polymerization as a stabilizer [130].

Other controlled radical polymerization methods were also employed for the synthesis of various block copolymers having poly(NVP) segment. ATRP of NVP using methyl 2-chloropropionate/5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclo-tetradecane (Me_6Cyclam)/copper(I) afforded well-defined poly(NVP) with the chloride end group, which was employed as a macroinitiator for the synthesis of novel fluorescent amphiphilic copolymers by ATRP of *N*-methacryloyl-*N*′-(α-naphthyl)thiourea as a hydrophobic monomer [120]. Poly(NVP)s with well-defined macromolecular structure were prepared by organostibine-mediated living radical polymerization [115]. Diblock copolymers poly(St)-*b*-poly(NVP), poly(MMA)-*b*-poly(NVP), and poly(NVP)-*b*-poly(MMA) were successfully prepared by successive addition of corresponding monomers to the organostibine macromediators. Thermoresponsive diblock copolymers of poly(NIPAAm) and poly(NVP) were synthesized via organotellurium-mediated controlled radical polymerization (Scheme 17) [116]. Well-defined amphiphilic block copolymers of poly(VAc) and poly(NVP) were synthesized by cobalt-mediated radical polymerization using cobalt(II) acetylacetone [119]. It was demonstrated that the polymerization of NVP was effectively initiated by poly(VAc) macroinitiator by the cleavage of the Co—C bond, and controlled as assessed by the first-order kinetics and the increase in the molar mass of the poly(NVP) with the monomer conversion. These amphiphilic poly(VAc)-*b*-poly(NVP) block copolymers (M_n = 21,700–86,400, M_w/M_n = 1.20–1.49) were obtained, which were easily converted into the double hydrophilic poly(vinyl alcohol)-*b*-poly(NVP) counterparts by selective methanolysis of the poly(VAc) block. Cobalt-mediated radical coupling was also applied for the preparation of symmetrical poly(VAc)-*b*-poly(NVP)-*b*-poly(VAc) triblock



Scheme 17. Synthesis of poly(NIPAAm)-*b*-poly(NVP) by organotellurium-mediated controlled radical polymerization.

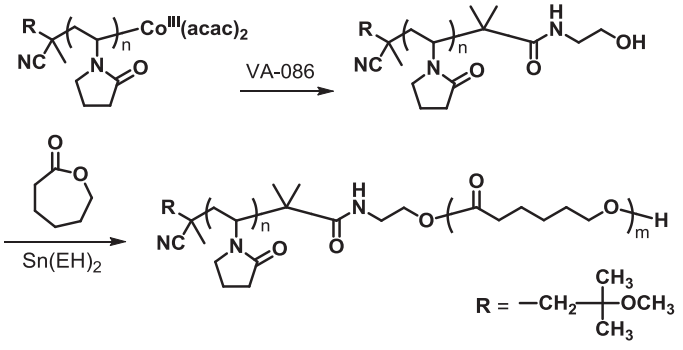


Scheme 18. Synthesis of poly(St)-*b*-poly(NVP) by the combination of ATRP and xanthate-mediated RAFT polymerization.

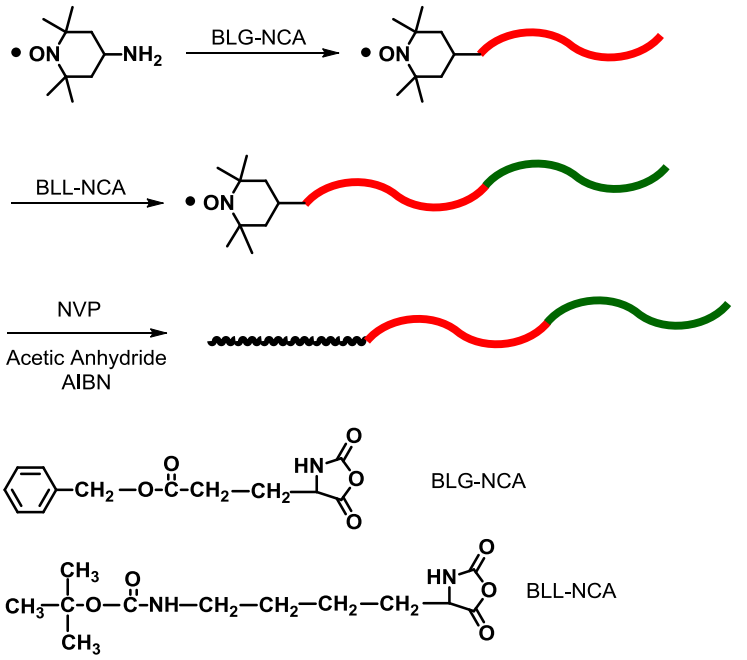
copolymers from the corresponding poly(VAc)-*b*-poly(NVP) diblock copolymer [131].

The synthesis of various block copolymers having poly(NVP) segment were conducted by combination of two different polymerization techniques. Amphiphilic diblock copolymers of poly(St) and poly(NVP) were prepared by a combination of ATRP and RAFT/MADIX (Scheme 18) [132]. In this system, well-defined poly(St) with bromine end group was synthesized by ATRP using (1-bromoethyl) benzene as an initiator. The Br-end group was then converted to xanthate, which was employed for the synthesis of poly(St)-*b*-poly(NVP) copolymers (M_n = 15,300–16,700, M_w/M_n = 1.5–1.6). Difunctional haloxanthate inifers were used for successive RAFT polymerization of NVP and ATRP of St, methyl acrylate, and MMA [133]. In the RAFT-first approach, well-controlled polymerization of NVP was observed using two chloroxanthate inifers (**Inifers 1–2**). Well-defined poly(NVP)-*b*-poly(St) ($M_{n,GPC}$ = 15,000 g/mol andM_w/M_n < 1.4) and poly(NVP)-*b*-poly(MMA) ($M_{n,GPC}$ = 50,600 g/mol and M_w/M_n < 1.3) were successfully synthesized through a subsequent chain extension by ATRP. In contrast, unexpected dimerization took place during the polymerization of NVP with the bromoxanthate inifers (**Inifers 3–4**). Controlled nitroxide-mediated and RAFT polymerization of NVP was also employed for the synthesis of block copolymers, poly(NVP)-*b*-poly(St) and poly(NVP)-*b*-poly(2-vinylpyridine) [113]. A combination of anionic and nitroxide-mediated radical polymerizations (dual initiator) was employed for the synthesis of poly(*n*-hexyl isocyanate)-*b*-poly(NVP) block copolymers [134].

The combination of controlled radical polymerization of NVP and ring-opening polymerization was also attractive methods to prepare various block copolymers. Poly(ε-caprolactone)-*b*-poly(NVP) block copolymers were synthesized by xanthate-mediated RAFT polymerization of NVP using poly(ε-caprolactone) macro-CTA, which was prepared by ring-opening polymerization of ε-caprolactone, followed by the end group modification with potassium *O*-ethyl xanthate [135]. The resulting block copolymers (M_n = 7600–15,800 and M_w/M_n = 1.42–1.52) had the xanthate CTA moiety on the chain end which was readily translated to hydroxyl or aldehyde for conjugating various functional moieties, such as fluorescent dye, biotin hydrazine and tumor homing peptide iRGD. Aldehyde ω-end-functional poly(NVP) was synthesized via quantitative conversion of a xanthate end-functional precursor obtained by RAFT-mediated polymerization [136]. The aldehyde-endfunctional poly(NVP) was successfully coupled with the model protein, lysozyme, via reductive amidation. An amphiphilic block copolymer of poly(NVP)-*b*-poly(ε-caprolactone) was also synthesized by a combination of cobalt-mediated radical polymerization and ring-opening polymerization (Scheme 19) [137]. In this system, the poly(NVP) prepared by cobalt-mediated radical polymerization was reacted with 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086) to modify its cobalt complex chain end to a hydroxyl group. The ring-opening polymerization of ε-caprolactone was subsequently carried out using the produced hydroxyl-terminated macroinitiator to afford block copolymes having relatively low polydispersities (M_n = 18,000–33,400 and M_w/M_n = 1.35–1.38). Similarly, poly(ε-caprolactone)-*b*-poly(NVP) block copolymers were synthesized via RAFT polymerization of NVP from xanthate-terminated poly(ε-caprolactone) macro-CTA, which was prepared by ring-opening polymerization of ε-caprolactone, followed by the transformation of the —OH end group into its corresponding xanthate [138]. The photoinitiated cobalt-mediated radical polymerization was also employed for the synthesis of α-functional and α,ω-telechelic poly(NVP)s [139]. In combination with ring-opening polymerization, the hydroxyl-terminated macroinitiators produced amphiphilic copolymers composed of poly(ε-caprolactone) and poly(NVP).



Scheme 19. Synthesis of poly(NVP)-*b*-poly(ε-caprolactone) by a combination of cobalt-mediated radical polymerization and ring-opening polymerization.



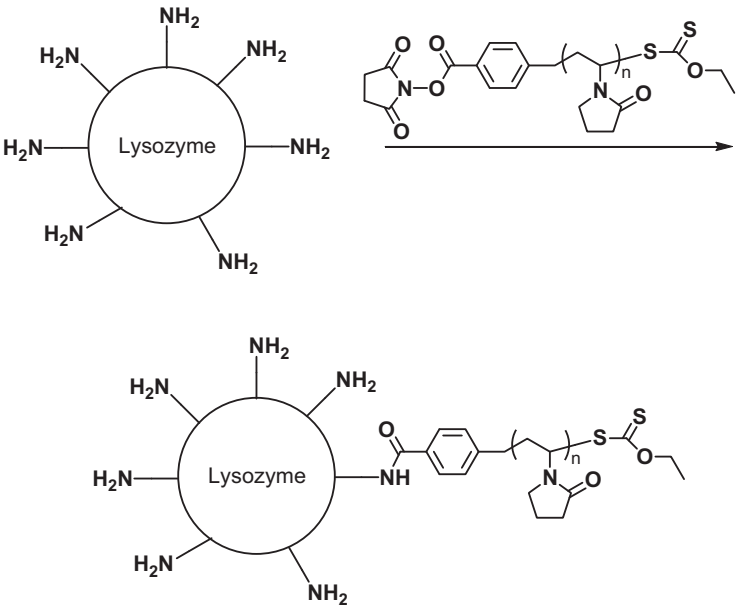
Scheme 20. Synthesis of poly(NVP)-*b*-poly(γ-benzyl-L-glutamate)-*b*-poly(*tert*-butyloxycarbonyl-L-lysine) by the combination of NMP and ring-opening polymerization.

Diblock and triblock copolymers of poly(NVP) and polypeptides, poly(NVP)-*b*-poly(γ-benzyl-L-glutamate), poly(NVP)-*b*-poly(*tert*-butyloxycarbonyl-L-lysine), poly(NVP)-*b*-poly(γ-benzyl-L-glutamate)-*b*-poly(*tert*-butyloxycarbonyl-L-lysine), were synthesized by the combination of NMP and ring-opening polymerization (Scheme 20) [140]. In the system, the amino-groups were used for the ring opening polymerization of α-amino acid carboxyanhydrides, while TEMPO was employed for the polymerization of NVP. The amphiphilic block copolymers composed of poly(NVP) as the hydrophilic polymer and poly(γ-benzyl-L-glutamate) as a hydrophobic polypeptide were also prepared using thiazolidine chemistry [141]. As a first step, ω-aldehyde end-functional poly(NVP) and cysteine end-functional poly(γ-benzyl-L-glutamate) were prepared. The latter makes use of a modified deprotection step for the thiol-protecting acetamidomethyl group. The self-assembly behavior and pH dependence of the bioconjugate was demonstrated.

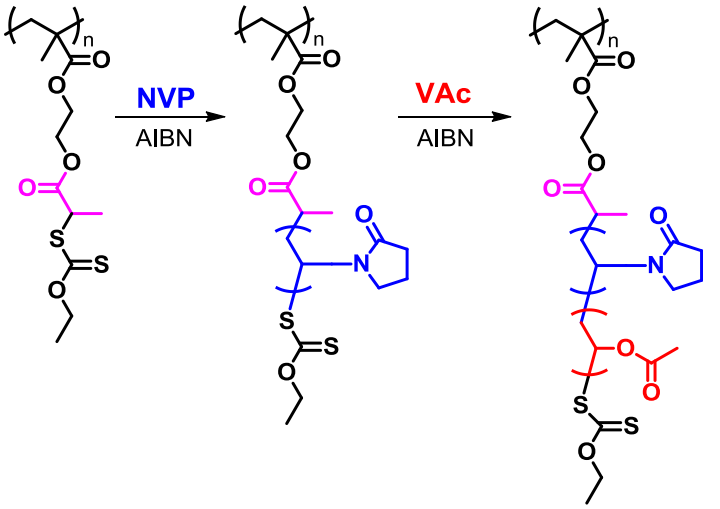
Poly(β-benzyl-L-aspartate)-*b*-poly(NVP) diblock copolymers having both hydrophobic and hydrophilic segments of various lengths were synthesized by a combination of radical polymerization with alcohol and ring-opening polymerization [142]. In vitro release behavior of prednisone acetate was investigated, which showed a dramatic responsive fast/slow switching behavior according to the pH-responsive structural changes of a micelle core structure. Similarly, poly(NVP)-*b*-poly(ε-caprolactone)s were synthesized by ring-opening polymerization of ε-caprolactone from hydroxyl-terminated poly(NVP), which was prepared by radical polymerization of NVP with 2-mercaptoethanol as a conventional CTA [143]. Another example involves the synthesis of A–B–A type amphiphilic triblock copolymer, poly(NVP)-*b*-poly(ε-caprolactone)-*b*-poly(NVP) by free radical polymerization of NVP in the presence of a α,ω-poly(ε-caprolactone) dithiol, which belongs to a traditional macromolecular chain-transferring agent [144]. Levia et al. also reported the synthesis of three-arm amphiphilic star block copolymers by free radical polymerization of NVP from three-arm poly(ε-caprolactone) star with thiol-end groups [145]. These synthetic approaches could be regarded as one of the useful approaches to synthesize poly(NVP)-containing block copolymers, even though the poly(NVP) segments were formed by free radical polymerization.

The RAFT process was highly versatile for the synthesis of novel polymer architectures involving poly(NVP) components, such as star polymers, graft copolymers, and hybrids. Using xanthate-type tetrafunctional CTA (**R-CTA 2**), poly(NVP) star with narrow molecular weight distributions (PDI < 1.3) were obtained [121]. Various pathways to synthesize star polymers based on RAFT/MADIX process of NVP was discussed [146]. A poly(NVP) seven-arms star polymer with lysozyme core was synthesized by conjugating linear *N*-succinimidyl ester terminated poly(NVP) to lysozyme (Scheme 21) [147]. Initially, reactive poly(NVP)s were synthesized using a RAFT agent functionalized with *N*-succinimidyl ester (**CTA 20**). The poly(NVP) was conjugated to lysozyme resulting in the attachment of seven poly(NVP)s to one lysozyme core.

Synthesis and characterization of five-arms star polymer of NVP through ATRP based on glucose were reported recently [148]. The ratio of reactants were kept as 1:1:2:200 (initiator:Cu(I)Br:bpy:NVP). The product showed narrow molecular weight distributions between 1.11–1.41. Well-defined nonlinear multiresponsive, multihydrophilic block copolymers, poly(NIPAAm)$_2$-[poly(NVP)-*b*-poly(acrylic acid)]$_2$ and poly[NIPAAm-*b*-(acrylic acid)]$_2$-poly(NVP)$_2$,



Scheme 21. Synthesis of poly(NVP) seven-arms star polymer with lysozyme core.



Scheme 22. Synthesis of molecular bottlebrushes with poly(NVP) and poly(NVP)-*b*-poly(VAc) side chains via a combination of ATRP and RAFT polymerization.

were successfully synthesized via a combination of SET-LRP and RAFT polymerization techniques [149]. A tetra-functional bromoxanthate inifer (**Inifer 6**, Xanthate$_2$-Br$_2$) was employed for the synthesis of miktoarm stars consisting of thermoresponsive poly(NIPAAm), pH-responsive poly(acrylic acid), and water-soluble and biocompatible poly(NVP).

Well-defined molecular bottlebrushes with poly(NVP) and poly(NVP)-*b*-poly(VAc) side chains were prepared via a combination of ATRP and RAFT (Scheme 22) [150]. A macro-CTA, poly(2-((2-ethylxanthatepropanoyl)oxy)ethyl methacrylate), was prepared by attaching xanthate moiety onto each monomeric unit of poly(2-hydroxyethyl methacrylate). Subsequently, RAFT polymerization procedure was used to synthesize molecular bottlebrushes with poly(NVP) side chains with controlled molecular weight and low polydispersity by grafting from the backbone. The side chains were then chain extended with poly(VAc), yielding a bottlebrush macromolecule with poly(NVP)-*b*-poly(VAc) side chains.

The synthesis of poly(vinylidene fluoride)-*g*-poly(NVP) copolymers via RAFT-mediated process and their use in antifouling and antibacterial membranes were reported [151]. The pore size and distribution varied with the grafting concentration and the density of graft points. A significant decrease of the amounts of adsorbed protein

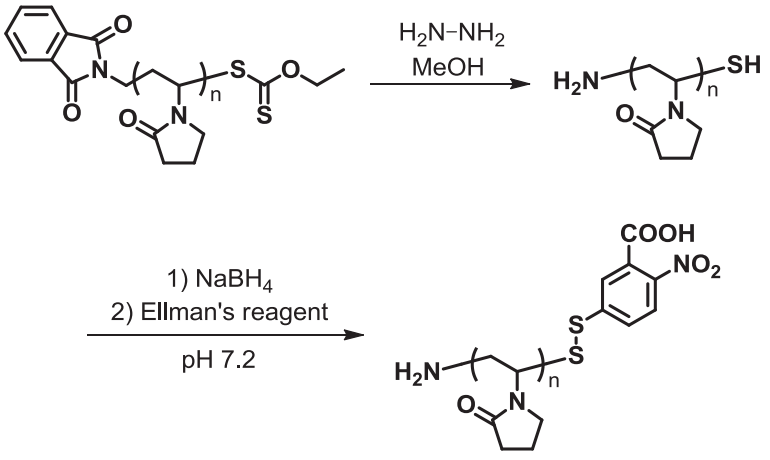
indicated improved antifouling properties. The microfiltration membranes were further functionalized via surface-initiated block copolymerization with (2-dimethylamino)ethyl methacrylate, followed by quaternization of the tertiary amine groups. The poly(NVP)-modified nonwoven fabric membranes were prepared by the grafting of poly(NVP) via the ATRP method [152]. The product exhibited improved antifouling properties.

Poly(NVP) was grafted onto crosslinked poly(St) beads through the 2-chloroethyl sulfonamide groups present in the resin using ATRP method [153]. The resulting grafted resin material showed an efficient sorbent for removal of dyes from water. Physically crosslinked polyurethane-*b*-poly(NVP) hydrogel biomaterials were synthesized by the macroiniferter controlled radical polymerization method [154]. The products exhibited successful tissue repair and regeneration, due to mediate cell interaction without inflicting undesirable responses. Functionalization of disulfide-stabilized poly(methacrylic acid) hydrogel was achieved by RAFT polymerization of poly(NVP), which introduced biorelevant heterotelechelic end groups (thiol and amine) to the polymer chain (Scheme 23) [155]. In the process, **CTA 19** was employed for the RAFT polymerization of NVP. In the last step, the Ellman's reagent was allowed to react with the thiol functionality for the characterization and storage purposes. The approach was a generic and versatile method for functionalization of disulfide-stabilized hydrogel capsules with macromolecules, including a number of specific antibodies to cancer cells.

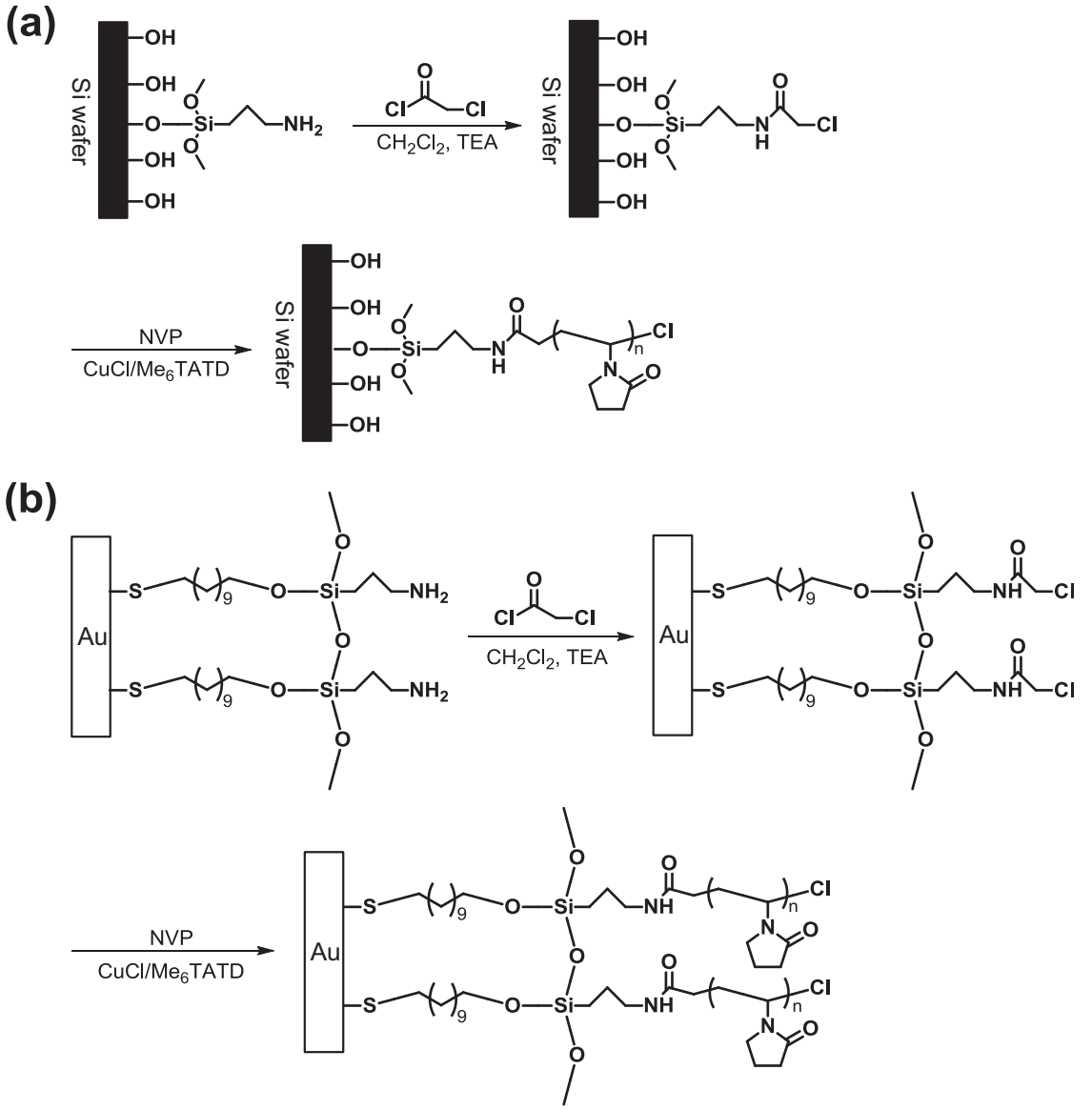
Surface modification with poly(NVP) has been investigated extensively over the past few years as a means of preventing nonspecific protein adsorption [156]. Well-controlled poly(NVP)-grafted silicon surfaces were prepared by surface-initiated ATRP with 1,4-dioxane/water mixtures as solvents and CuCl/5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (Me_6TATD) as a catalyst (Scheme 24a) [157]. They demonstrated that a poly(NVP)-modified silicon surfaces reduced the level of adsorption of fibrinogen, human serum albumin, and lysozyme, respectively. The same approach, surface-initiated ATRP, was also employed for the preparation of poly(NVP)-*b*-poly(St) modified glass surfaces [158]. Well-controlled polymerization of NVP on gold surfaces by surface-initiated ATRP was carried out at room temperature by a silanization method (Scheme 24b) [159]. Initially, the method was employed to form an adhesion layer for initiator attachment, which allowed well-defined ATRP polymerization to occur on Au surfaces.

N-Vinylcaprolactam (NVCL) is another cyclic vinyl amide with a seven-membered lactam ring, and belongs to a typical nonconjugated monomer that undergoes polymerization only radically. NVCL is structurally similar to NVP, for alkene *p*-electrons are not conjugated with the C=O functional group. Poly(NVCL) is a nonionic, nontoxic, water soluble, thermally sensitive and biocompatible polymer. It contains hydrophilic carboxylic and amide groups with hydrophobic carbon–carbon backbone suitable for biomedical applications. Desavia et al. initially reported RAFT polymerization of NVCL using a xanthate-type CTA (**CTA 4**) for the synthesis of poly(NVCL)-*b*-poly(NVP) [160], while no details were included. Then, controlled radical polymerization of NVCL mediated by xanthate or dithiocarbamate was reported, employing **CTA 1**, **CTA 2**, and **CTA 32** [161]. These three CTAs led to the controlled radical polymerization of NVCL, with the molecular weight increased along with the conversion and relatively narrow molecular weight distributions ($M_w/M_n < 1.5$) could be obtained. They also reported the synthesis of poly(VAc)-*b*-poly(NVCL) having lower polydispersities ($M_w/M_n = 1.30–1.37$), in which the polymerization of NVCL was conducted using poly(VAc) macro-CTA prepared with **CTA 32**. Shao et al. also reported RAFT polymerization of NVCL using either **CTA 44** or **CTA 34** [162]. They demonstrated that the cloud point temperatures of poly(NVCL) were shifted to lower temperature and concentrations as the hydrophobicity of the end groups and the molecular weights of the polymers increased.

Thermo-responsive block copolymers based on poly(NVCL) have been prepared by cobalt-mediated radical polymerization [163]. The homopolymerization of NVCL was controlled by *bis*(acetylacetonato)cobalt(II). The



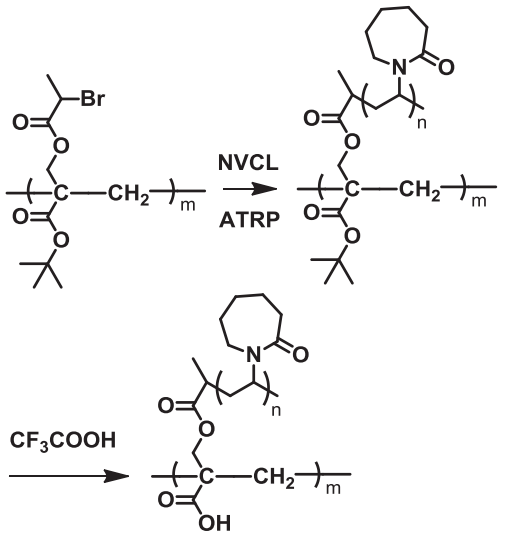
Scheme 23. End-group transformation of poly(NVP) prepared by RAFT polymerization.



Scheme 24. Surface-initiated ATRP of NVP from (a) silicon and (b) gold surfaces.

polymerization of NVCL was also initiated from a poly(VAc)-$Co(acac)_2$ macroinitiator to yield well-defined poly(VAc)-*b*-poly(NVCL) block copolymers with a low polydispersity (M_w/M_n = 1.1) up to high molecular weights (M_n = 87,000). The amphiphilic block copolymers were hydrolyzed into unprecedented double hydrophilic poly(vinyl alcohol)-*b*-poly(NVCL) having characteristic temperature-dependent solution behavior. Kermagoret et al. also reported cobalt-mediated radical copolymerization of NVCL and hydrophilic vinylamides (*N*-methyl-*N*-vinylacetoamide (NMVA), *N*-vinylacetoamide (NVA)) and hydrophobic vinylesters (VAc and vinyl pivalate) to afford narrowly distributed NVCL-based copolymers [164]. The LCST of the copolymers could be precisely tuned up and down by incorporating increasing amounts of vinylamides and vinylesters. Poly(NVCL)-containing block copolymers having two discrete LCSTs were also synthesized following a one-pot strategy based on the sequential cobalt-mediated polymerization of NVCL followed by the copolymerization of NMVA with the residual NVCL.

Triple-shell architectures, consisting of poly[(*N*,*N*-diethylaminoethyl methacrylate)-*b*-(NVCL)-*b*-(*N*,*N*-dimethylaminoethyl methacrylate)] triblock copolymers, were obtained by sequential RAFT polymerizations, using a terminal-modified hyperbranched poly(β-cyclodextrin) core as a macro-CTA [165]. The products exhibited star-like structures having multiresponsive (pH- and dual thermoresponsive) triblock copolymers as arms. A series of well-defined amphiphilic graft copolymers consisting of a hydrophobic poly(*tert*-butyl acrylate) backbone and hydrophilic poly(NVCL) side chains were synthesized via the combination of RAFT polymerization, ATRP, and the



Scheme 25. Synthesis of graft copolymers having hydrophilic poly(NVCL) side chains via the combination of RAFT polymerization and ATRP, followed by hydrolysis.

grafting-from strategy without any polymeric functional transformation (Scheme 25) [166]. Finally, the hydrophobic poly(*tert*-butyl acrylate) backbone was selectively hydrolyzed into a hydrophilic poly(acrylic acid) without affecting poly(NVCL) side chains in the acidic environment to provide double-hydrophilic graft copolymers.

ATRP of NVCL was studied by using ethyl-2-bromoisobutyrate as initiator and Cu(I)Br/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) in 1,4-dioxane [167]. Under the suitable conditions ([NVCL]/[Initiator]/[CuBr]/[PMDETA] = 50:1:1:1), the molecular weight increased along with the conversion of monomer and relatively narrow molecular weight distributions (M_w/M_n = 1.21-1.40) could be obtained. The living nature of the ATRP for NVCL was confirmed by the experiments of poly(NVCL) chain extension. Self-assembling of the amphiphilic poly(NVCL) homopolymer led to the formation of their micellar aggregates in aqueous media. The poly(NVCL)/silver nanocomposite exhibited strong antibacterial activity against *Enterococcus faecalis*.

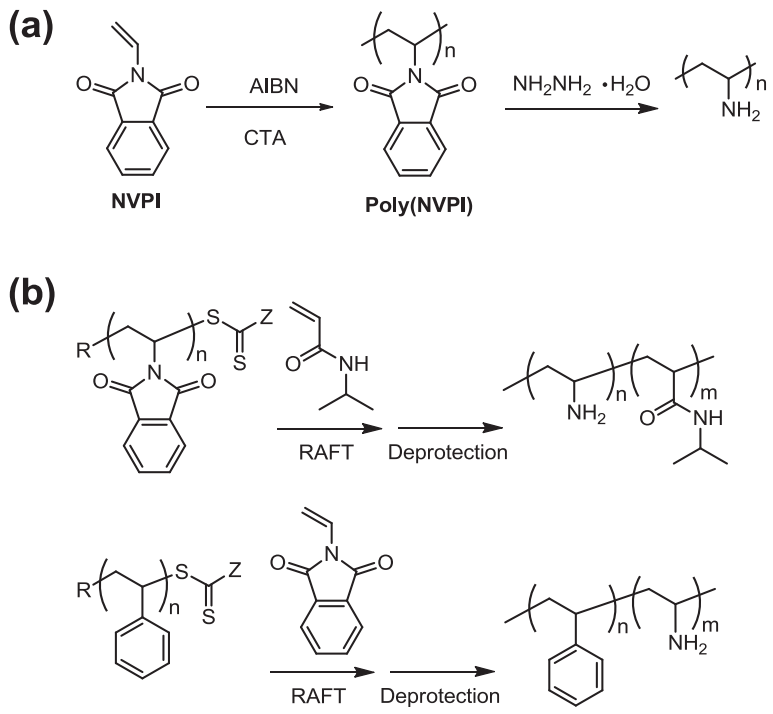
Recently, Beija et al. reported the synthesis of narrowly distributed poly(NVCL) obtained by the MADIX/RAFT process and their applications for novel thermoresponsive gold nanoparticles presenting a sharp reversible response to temperature [168]. Using a xanthate-type CTA (**CTA 4**), poly(NVCL) with M_n values up to 150,000 and low polydispersities (M_w/M_n < 1.2) were synthesized. The poly(NVCL)/gold nanohybrids exhibited a sharp and reversible response to the temperature, which can be easily modulated near the physiological temperature by simply changing the polymer molecular weight or concentration.

Although a variety of controlled radical polymerization techniques have been successfully applied for cyclic *N*-vinyl amides (NVP and NVCL), the control of radical polymerization of noncyclic *N*-vinyl amides derivatives was demonstrated to be not straightforward. In fact, limited articles have been published so far for controlled radical polymerization of noncyclic *N*-vinyl amides derivatives, involving *N*-vinylformamide (NVF), *N*-vinylacetoamide (NVA), and *N*-methyl-*N*-vinylacetoamide (NMVA). Poly(ethylene glycol)-*b*-poly(NVF) copolymers were synthesized by the RAFT polymerization of NVF using a xanthate-terminated macro-CTA (**CTA 18**) [169]. In the system, the molecular weights and NVF monomer conversion increased with increasing the polymerization time, while resulting block copolymers exhibited broad molecular weight distributions (M_w/M_n > 1.7). The cobalt-mediated radical polymerization of NMVA afforded well-defined poly(NMVA)s with low polydispersities (M_w/M_n = 1.1–1.2) [170]. It was demonstrated that the amide moiety of the last monomer unit of the chain chelates the cobalt, which reinforces the cobalt–polymer bond in the order NVP < NVCL < NMVA, and stabilizes the dormant species. They also reported that the homopolymerizations of the secondary *N*-vinyl amides (NVF and NVA) suffered from either poor or no control, whereas copolymerization of NMVA with NVA proceeded in a controlled fashion. As mentioned above, the synthesis of narrowly distributed NVCL-based copolymers by cobalt-mediated radical copolymerization of NVCL and *N*-vinylamides (NMVA and NVA) was also reported [164].

4. *N*-vinylphthalimide (NVPI) and *N*-vinylnaphthalimide (NVNPI)

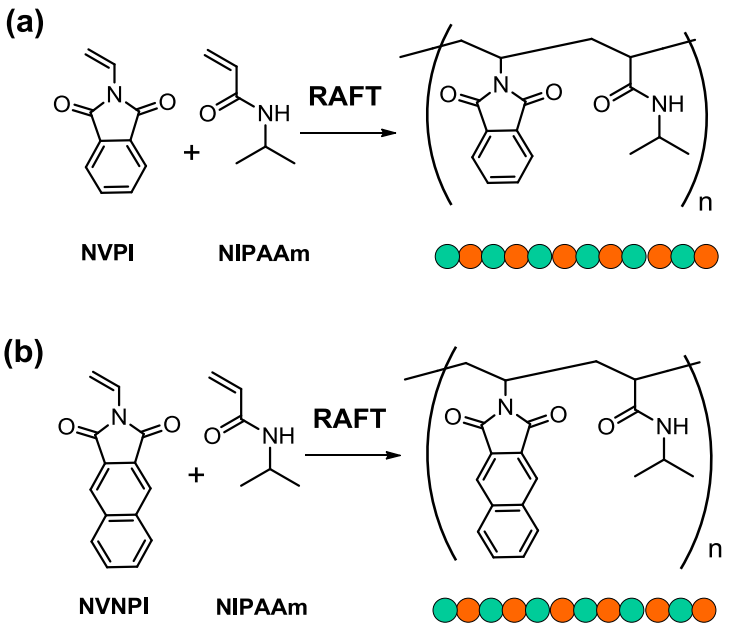
Phthalimides belong to nitrogen-containing heterocyclic compounds, which are important components of many natural and synthetic products with wide range of properties. The phthalimide groups have also provided the classical means for direct introduction of the masked amino functions as well as for *N*-protection of amino acids, amino sugars, and simple amino alcohols [171]. A variety of polymers having phthalimide moieties in the side chains, including poly(*N*-vinylphthalimide), have been reported [172]. Free radical polymerization of *N*-vinylphthalimide (NVPI) was reported to proceed in the presence of conventional radical initiator, and various copolymers composed of NVPI were synthesized by this method [173]. Attempts to synthesize well-defined polymers containing phthalimide groups using controlled radical polymerizations have appeared in the literature. For example, a St derivative having a phthalimide, *N*-(p-vinylbenzyl) phthalimide was employed as a functional monomer for the synthesis of St-based block copolymers by NMP [174,175] and ATRP [176]. Recently, phthalimide-containing CTA was used for RAFT polymerization, and the phthalimide chain end was transformed quantitatively into the primary amine structure [177–179].

The stabilizing effect of NVPI (Q = 0.36, e = −1.52)[180] is comparable to that of NVC (Q = 0.26, e = −1.29)[55] with a higher electron-donating property, while the Q value is slightly lower than that of NVP (Q = 0.53, e = −1.30) [55]. Similar to propagating radicals derived from NVC and NVP, the NVPI propagating radical is a reactive species having a higher electron density at the radical center. Therefore, the fragmentation of the adduct radical (intermediate RAFT radical) is thought to be slow, resulting in insufficient



Scheme 26. Synthesis of (a) well-defined poly(vinyl amine) and (b) amphiphilic and double-hydrophilic block copolymers having poly(vinyl amine) segments using RAFT polymerization of *N*-vinylphthalimide (NVPI), followed by deprotection.

control of the polymerization. Controlled radical polymerization of a nonconjugated *N*-vinyl monomer, NVPI, was attained using the xanthate-type RAFT agents (**CTA 5** and **CTA 6**) and dithiocarbamate-type one (**CTA 21**) [181]. These CTAs were the most efficient to obtain poly(NVPI) with controlled molecular weights and low polydispersities (M_n = 4100–13,000, and M_w/M_n = 1.29–1.38). Good control of the polymerization was confirmed by the molecular weight controlled by the monomer/CTA molar ratio, linear increase in the molecular weight with the polymer yield, and the ability to extend the chain by the second addition of the monomer. Deprotection of the phthalimide groups



Scheme 27. Synthesis of alternating copolymers by RAFT copolymerization of *N*-isopropylacrylamide (NIPAAm) with (a) *N*-vinylphthalimide (NVPI) and (b) *N*-vinylnaphthalimide (NVNPI).

in poly(NVPI) using hydrazine monohydrate gave water-soluble poly(vinyl amine) (Scheme 26a).

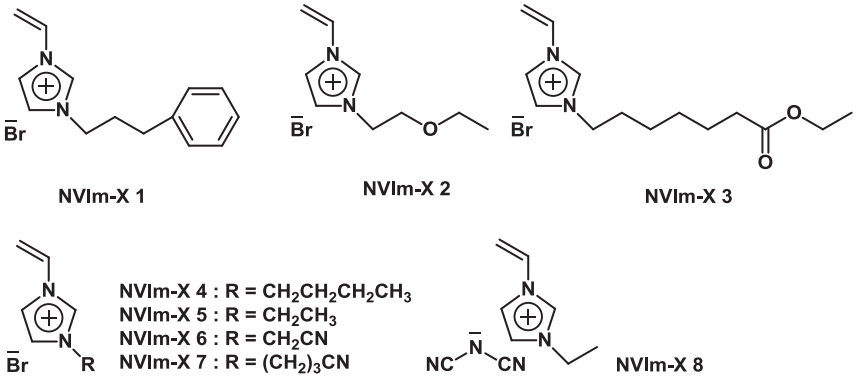
Synthesis of amphiphilic and double-hydrophilic block copolymers having poly(vinyl amine) segments was conducted by RAFT polymerization of NVPI, followed by deprotection (Scheme 26b) [182]. The chain extension from the dithiocarbamate-terminated poly(St) to NVPI could be controlled well under suitable conditions and provided the block copolymer, poly(St)-*b*-poly(NVPI). The block copolymer poly(NVPI)-*b*-poly(NIPAAm) with a controlled molecular weight and low molecular mass distribution was obtained by the polymerization of NIPAAm using dithiocarbamate-terminated poly(NVPI). These double-hydrophilic and amphiphilic block copolymers obtained after deprotection exhibited characteristic thermoresponsive and optoelectronic properties and the aggregation behavior. RAFT copolymerization of NVPI and NIPAAm using the dithiocarbamate-type mediating agent (**CTA 21**) afforded well-defined copolymers with predominantly alternating structure, controlled molecular weights, and low molecular mass distributions (Scheme 27a) [183]. RAFT polymerization of NVPI was also carried out using a trithiocarbonate-type CTA (**CTA 41**) for the preparation of ultrafine microfibers by electrospinning technique [184]. Using the system, the molecular weights of poly(NVPI) increased linearly with the monomer conversion and the molecular weight distributions were relatively narrow (PDI < 1.2).

Naphthalenic imides are an important and a versatile class of heterocyclic compounds, which have been applied in a large variety of areas. For example, 2,3-naphthalimide and 1,8-naphthalmide were used as fluorescent compounds in the biological fields, such as probes for monitoring peptide binding to histocompatibility complex proteins [185], selective opioid peptides [186], and environment-sensitive fluorescent probe for peptide-peptide interactions [187]. Recently, the synthesis of novel naphthalimide-containing copolymers with controlled molecular weights and narrow polydispersity was achieved by copolymerization of a nonconjugated *N*-vinyl monomer, *N*-vinylnaphthalimide (NVNPI), via RAFT process [188]. The sufficient incorporation of NVNPI was achieved during the RAFT copolymerization, when methyl acrylate, *N*,*N*-dimethylacrylamide, and NIPAAm were used as comonomers. In particular, the copolymerization of NVNPI and NIPAAm using the dithiocarbamate-type mediating agent (**CTA 21**) afforded well-defined copolymers with a predominantly alternating structure, controlled molecular weights, and low molecular mass distributions (Scheme 27b).

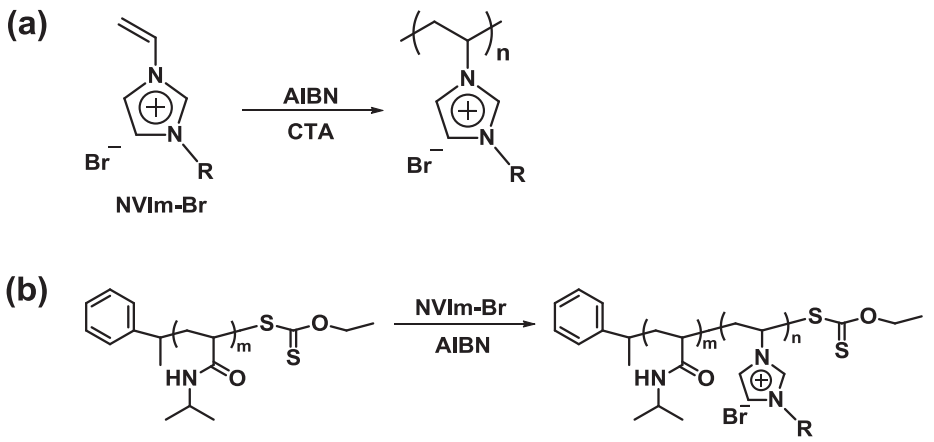
5. *N*-vinylimidazolim salts (NVIm-X) and *N*-vinylimidazole (NVIm)

Recently, much attention has been paid to polymerized ionic liquids or polymeric ionic liquids, which are macromolecules obtained from polymerizing ionic liquid monomers [189–191]. An attractive feature of polymeric ionic liquids is the fact that unique and attractive properties can be tuned widely by adjusting the structures of the cation (e.g., imidazolium, pyridinium, and tetraalkylammonium) and the anion (e.g., halide, tetrafluoroborate, hexafluorophosphate). Their potential applications involve polymeric electrolytes, catalytic membranes, ionic conductive materials, CO_2 absorbing materials, microwave absorbing materials, porous materials, and so on. Among various ionic liquids, imidazolium salt is the most popular cation which has been induced into polymer backbone. A variety of polymers having imidazolium moieties in the side chains, including poly(*N*-vinyl imidazolium) derivatives [192–195], have been reported, and most of these poly(ionic liquid)s were prepared by conventional radical polymerizations.

Recent significant progress of controlled radical polymerization has allowed for the synthesis of well-defined block copolymers containing the imidazolium moieties [105,196]. For example, Waymouth et al. demonstrated the synthesis of a series of block copolymers comprising a poly(St) and an imidazolium-functionalized poly(St) by NMP, followed by postsynthesis modification of the chloromethyl group [197,198]. Gnanou et al. reported the synthesis of double hydrophilic block copolymers having ionic responsive property by RAFT polymerization of methacrylate-type ionic liquids [199]. RAFT polymerization was also employed for the synthesis of block copolymers composed of the imidazolium-containing mathacrylate and thiazole-containing methacrylamide, which showed characteristic



Scheme 28. Structures of *N*-vinyl imidazolium salts used for controlled radical polymerizations.

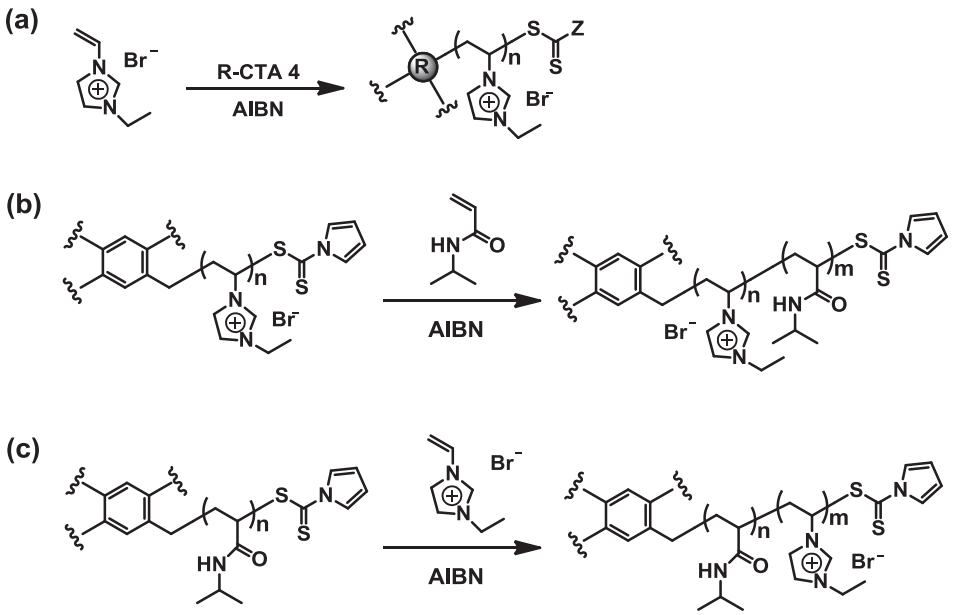


Scheme 29. Synthesis of (a) poly(*N*-vinylimidazolium salt)s by RAFT polymerization of *N*-vinylimidazolium salts and (b) thermoresponsive-ionic block copolymers by RAFT polymerization of *N*-vinylimidazolium salts using poly(NIPAAm) as a macro-CTA.

magnetic properties [200]. Other examples involve RAFT polymerization of methacrylate derivatives having imidazolium moieties [201,202] and ATRP of St derivatives [203].

Recently, a variety of *N*-vinylimidazolium salts (Scheme 28), which belong to *N*-viny monomers, have been employed for controlled radical polymerizations. In 2007, we reported the controlled synthesis of poly(*N*-vinylimidazolium salt)s with narrow molecular weight distribution, predetermined molecular weight by RAFT/MADIX polymerization of *N*-vinylimidazolium salts (NVIm-Xs 1–3) (Scheme 29a) [204]. Two xanthate-type CTAs (**CTA 2** and **CTA 5**) proved efficient for obtaining poly(*N*-vinylimidazolium salt)s with relatively low polydispersities (M_w/M_n < 1.4). The structure of the substituent group on the imdazolium ring (NVIm-Xs 1–3) affected the polymerization behavior and solubilities of the resulting poly(*N*-vinylimidazolium salt)s. Polymerizations of the *N*-vinylimidazolium salts using the dithiocarbonate-terminated poly(NIPAAm) as a macro-CTA provided well-defined thermoresponsive-ionic block copolymers (Scheme 29b), which showed characteristic thermally-induced phase separation behavior and assembled structures in aqueous solution.

Yuan et al. also reported RAFT synthesis of double hydrophilic diblock copolymers containing a poly (*N*-vinylimidazolium salt) segment using the dithiocarbon-



Scheme 30. Synthesis of (a) poly(*N*-vinylimidazolium salt) stars by RAFT polymerization of *N*-vinylimidazolium salt (NVIm-X 5) using tetrafunctional CTAs, and thermoresponsive-ionic star block copolymers by (b) RAFT polymerization of NIPAAm using poly(NVIm-X 5) star as macro-CTA, and (c) RAFT polymerization of NVIm-X 5 using poly(NIPAAm) star as macro-CTA.

ate-terminated poly(NIPAAm) or poly(*N*,*N*-dimethylacrylmide) as a macro-CTA [205]. Using four different *N*-vinylimidazolium salts (NVIm-Xs 5–8), various poly(NIPAAm)-*b*-poly(ionic liquid)s were obtained, which were dual stimuli-responsive block copolymers that can respond to the changes in temperature and ionic strength in aqueous solution. It was demonstrated that the chain extension reaction was affected significantly by the size of counter anion. The block copolymer was also employed as carbon precursor for the preparation of mesoporous graphitic nanostructures in the presence of metal salts. Recently, Wang et al. reported the detailed investigations of the assembly properties, thermal phase behavior and microdynamics of poly(NIPAAm)-*b*-poly(NVIm-X 4) prepared by the RAFT/MADIX polymerization, in aqueous solution [206].

The cobalt-mediated radical polymerization of *N*-vinylimidazolium salt (NVIm-X 5) under mild conditions was reported recently by Detrembleur et al. [207]. They demonstrated that excellent control over molecular weights and dispersities (M_w/M_n = 1.05–1.06) was achieved in methanol, with a linear increase of experimental molecular weights with the monomer conversion. Diblock copolymers composed of poly(VAc) and poly(ionic liquid) were then obtained by sequential cobalt-mediated radical polymerization. Cobalt mediated radical coupling of the aforementioned diblock copolymers, using isoprene as a simple coupling agent, led to well-defined poly(VAc)-*b*-poly(NVIm-X 5)-*b*-poly(VAc).

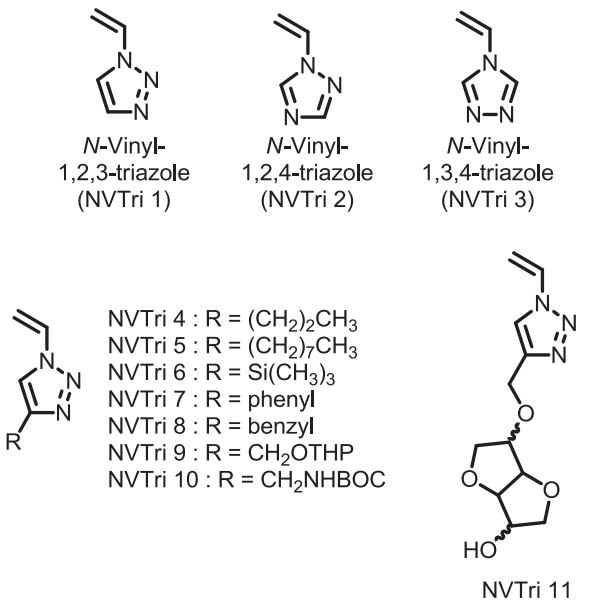
Star block copolymers comprising poly(*N*-vinylimidazolium salt) as a poly(ionic liquid) segment and poly(NIPAAm) as a thermoresponsive segment were also synthesized by RAFT polymerization [208]. The dithiocarbamate-type tetrafunctional CTA (**R-CTA 4**) was found to be the most efficient for the controlled synthesis of four-arm poly(NVIm-X 5) stars having low polydispersity and controlled molecular weights (Scheme 30a). Star block copolymers having inner thermoresponsive segments connected to the core were synthesized by RAFT polymerization of NVIm-X 5 using poly(NIPAAm) star (Scheme 30c). In contrast, RAFT polymerization of NIPAAm using poly(*N*-vinylimidazolium salt) star afforded star block copolymers with block arms consisting of outer block copolymer segment of the thermoresponsive poly(NIPAAm) (Scheme 30b).

Despite recent significant progress of controlled radical polymerization of various *N*-vinyl monomers, achieving controlled polymerization of *N*-vinylimidazole (NVIm) has remained largely unexplored. A few investigations have been reported on the topics. Double hydrophilic block copolymers, poly(NIPAAm)-*b*-poly(NVIm), were prepared with good control via RAFT process [209]. Initially, poly(NIPAAm) macro-CTA was prepared by RAFT polymerization with **CTA 2**, then the xanthate-terminated macro-CTA was employed for the polymerization of NVIm. The resulting double hydrophilic block copolymers showed low polydispersities (M_w/M_n = 1.15–1.25), which can serve as self-catalyzing nanoreactors [209]. Yamago et al. recently reported that UV–vis irradiation of an organotellurium chain transfer agent in the presence of NVIm led to the formation of highly controlled poly(NVIm) homopolymer with predetermined number average molecular weights and narrow molecular weight distribution [73]. In their review, Long et al. demonstrated that NMP utilizing a suitable nitroxide compound afforded the poly(NVIm)s with M_ns varying from targeted values and relatively large polydispersities (M_w/M_n > 1.4) [105].

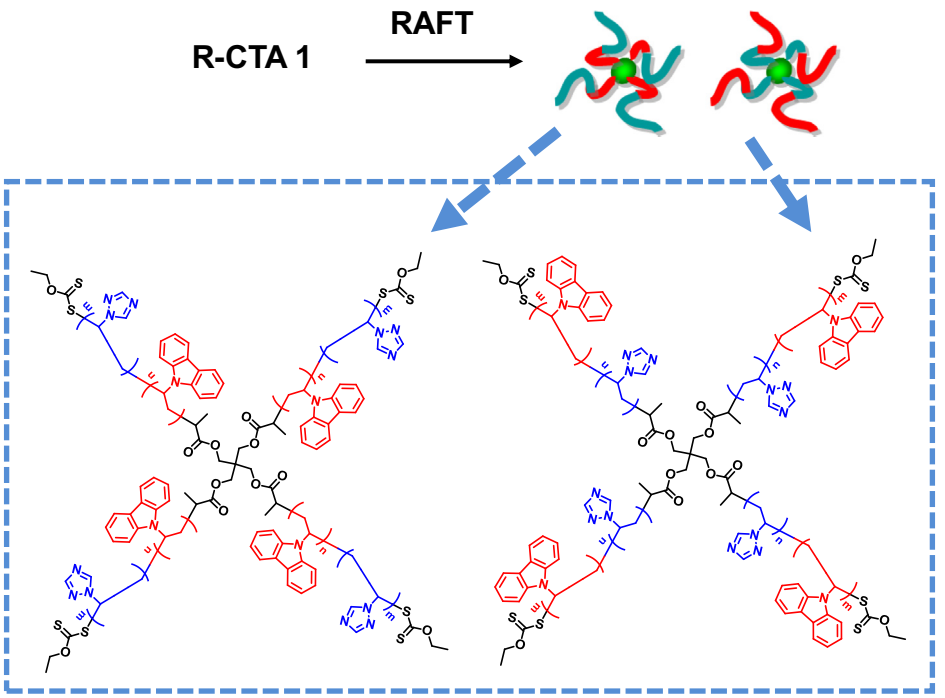
6. *N*-vinytriazole (NVTri)

Triazoles belong to highly stable heterocyclic compounds possessing an electron-rich aromatic ring prone to π–π interactions, nitrogen atoms available for hydrogen bonding or metal ion coordination, and a strong dipole moment. During recent years, considerable attention has been paid to functional polymers derived from *N*-vinyl-triazole derivatives (Scheme 31), which belong to vinylazoles. Kizhnyaev et al. reported the free radical polymerization behaviors of various vinylazoles and properties of the resulting poly(vinylazoles), involving poly(vinyldiazole)s, poly(vinyltriazole)s, and poly(vinyltetrazole)s. As to the solubility of poly(vinylazole)s, it was reported that water solubility of nonionogenic poly(vinyl azole)s is associated with the presence of basic nitrogen atoms of the pyridine type in the heterocycle that tend to form hydrogen bonds with water molecules [210]. *N*-vinyl-triazole can be classified into three monomers, *N*-vinyl-1,2,3-triazole (NVTri 1), *N*-vinyl-1,2,4-triazole (NVTri 2), and *N*-vinyl-1,3,4-triazole (NVTri 1), as shown in Scheme 31. Among them, poly(NVTri 2), having an isolated pyridine-type nitrogen atom in the heterocycle is soluble in water. In contrast, poly(vinylazole)s containing sequences of two or a large amount of nitrogen atoms in the heterocycle, such as poly(NVTri 1) and poly(NVTri 3), are insoluble in water.

Recently, the synthesis and polymerization of vinyl-1,2,3-triazoles have gained great attention driven by the remark-



Scheme 31. Structures of *N*-vinyl-triazole derivatives.



Scheme 32. Synthesis of amphiphilic star block copolymers by RAFT polymerization of *N*-vinyl-1,2,4-triazole (NVTri 2) with tetrafunctional CTA.

able development of the copper-catalyzed azide-alkyne cycloaddition, which is recognized as the most widely applied example of the "click" chemistry. Indeed, a broad library of *C*-vinyl and *N*-vinyl-1,2,3-triazole-based monomers and polymers carrying aliphatic, aromatic, heterocyclic or functional groups has been reported [211]. Recent significant progress of controlled radical polymerization has allowed for the synthesis of well-defined polymers from vinyl triazole-based monomers. For example, RAFT polymerization of various functional 4-vinyl-1,2,3-triazoles with pendant substituents, which were prepared by the "click" chemistry, was initially reported by Hawker's group [212]. The same group also reported the synthesis of isomeric, functionalized 4-vinyl-1,2,3-triazoles and 5-vinyl-1,2,3-triazoles, and RAFT polymerization of these *C*-vinyl-1,2,3-triazoles [213]. The "click" chemistry was also employed for the synthesis of 1-vinyl-1,2,3-triazoles derivatives, which belong to *N*-vinyltriazole. RAFT and NMP of 1-vinyl-1,2,3-triazoles derivatives (NVTris 4–10) having various substituent groups have allowed for the synthesis of functional polymers and block copolymers [214]. RAFT polymerization of bio-based 1-vinyl-4-dianhydrohexitol-1,2,3-triazole stereoisomer (NVTri 11) was also reported [215].

Recently, we also reported RAFT polymerization of *N*-vinyl-1,2,4-triazole (NVTri 2), which is a nonconjugated *N*-vinyl monomer having a basic aromatic heterocycle [216]. RAFT polymerization of NVTri 2 was found to proceed in a controlled fashion using a suitable xanthate-type mediating agent (**CTA 5**), resulting in the formation of well-defined water-soluble polymer [216]. Since poly(NVTri 2) possesses a basic nitrogen atom of the pyridine type in the heterocycle, it represents a class of water-soluble polymers and cationic polyelectrolytes. RAFT polymerization also afforded well-defined block copolymers comprising poly(NVTri 2) as a hydrophilic segment and a hydrophobic poly(NVC) with characteristic optoelectronic properties.

RAFT polymerization of NVTri 2 using R-designed tetrafunctional CTA having dithiocarbonate moieties as the Z groups (**R-CTA 1**) was employed for the controlled synthesis of water-soluble star polymers [217]. Four-arm amphiphilic star block copolymers with poly(NVTri) and poly(NVC) segments as separated inner and outer blocks and opposite sequence were also prepared by RAFT polymerization using the tetrafunctional xanthate-type CTA (Scheme 32). These amphiphilic star block copolymers form spherical micelles, inverse micelles, and aggregated structures, depending on the nature of the solvents. Assembled structures and optoelectronic properties of two series of star block copolymers are quite different and depend on the sequence of each block (location of the hydrophilic segment) along the arms of the stars.

7. Conclusion

This review has summarized the approaches to synthesis of a variety of tailor-made polymers by controlled radical polymerization of the nonconjugated *N*-vinyl monomers, which can be used as important class

of building and functional units. Considerable progress has been made in the last decade in the field of controlled radical polymerization of the *N*-vinyl monomers, which have allowed great advances in the design and synthesis of complex macromolecules, such as block and graft copolymers, star polymers, and polymer hybrids with unique functions and properties. Among various systems, RAFT polymerization using xanthate-type CTAs, organoheteroatom-mediated living radical polymerization, and cobalt-mediated radical polymerization were particularly useful to achieve controlled radical polymerization of *N*-vinyl monomers. Combination of two different polymerization techniques (RAFT and ATRP, RAFT and NMP, RAFT and ring-opening polymerization, and so on) offered the opportunity to develop characteristic block and graft copolymers and mikto-arm stars consisted of "more activated" and "less activated" monomers, as well as vinyl and cyclic monomers. The functional polymers derived from the *N*-vinyl monomers with well-defined architectures can provide viable tailored materials with unique properties for a wide range of applications.

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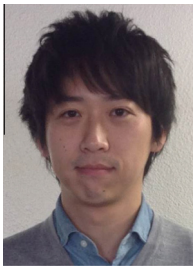

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